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THE

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I.—*On some new Colouring Matters, Derivatives of Dinitrobenzole, Dinitronaphthaline, &c. &c.*

By Arthur H. Church and William H. Perkin.

By the action of nascent hydrogen upon dinitrobenzole, its homologues and analogues, red or purple colouring matters of great intensity are produced. At present we can give an account of the preparation, composition, and properties of two only of these interesting bodies; but, as we shall show towards the conclusion of this communication, the number of similar bodies producible is very great.

I. *Action of nascent hydrogen on Dinitrobenzole.*—When an alcoholic solution of dinitrobenzole is treated with zinc and hydrochloric acid, the evolution of hydrogen, at first energetic, soon ceases almost entirely, and then the liquid in the immediate neighbourhood of the zinc assumes a rich crimson colour. When the reaction is complete, the liquid must be separated from any excess of zinc, and after complete neutralisation with an alkali, thrown upon a filter and washed with water. The dark-coloured oxide of zinc on the filter must be exhausted repeatedly with strong alcohol. The residue left on evaporation to dryness at 100° C. of this alcoholic solution, may be completely purified by washing with water and exhaustion with absolute alcohol, in which the colouring matter is extremely soluble. This solution evaporated in the water-bath ultimately deposits the whole of the colouring matter in a state of perfect purity. We have examined

the properties of the substance as obtained from its solution in absolute alcohol. For considerations which will shortly be apparent, we have named this substance NITROSOPHENYLINE. Besides the general outlines of the method for the preparation of nitrosophenyline, the following precautions may be noted. If the acid solution of the colouring matter be evaporated to dryness in the presence even of a trace of chloride of zinc, the substance then no longer gives with strong acids the characteristic magnificent crimson tint of nitrosophenyline. Again, the action of the zinc must not be too energetic, nor must the solution get too hot. A saturated cold solution of dinitrobenzole may be taken; the zinc should be perfectly pure, and in the form of a long strip, which, when occasion requires, may be conveniently and rapidly withdrawn. The hydrochloric acid should be strong, and added carefully, drop by drop, until the whole of the dinitrobenzole has been converted: when the reaction is complete, a drop of the coloured solution will not produce any turbidity with water.

Properties of Nitrosophenyline.—As obtained by the evaporation of its alcoholic solution, nitrosophenyline occurs in the form of a black, shining film, brittle, and easily removed from the containing vessel. Although when pure it stands a temperature considerably higher than 100° C. without undergoing any change, yet it is not volatile without decomposition. On the application of heat, it fuses, then evolves a white vapour, leaving a very bulky carbonaceous residue, which may be completely burnt in a stream of oxygen or by prolonged ignition in the air. The new body is almost insoluble in water, but very soluble in acids and in alcohol. To benzole, &c., it imparts scarcely a trace of colour. Heated strongly with soda-lime, all the nitrogen of nitrosophenyline appears in the forms of ammonia and aniline. The formation of aniline was detected by its well-known reaction with hypochlorite of lime. Nitrosophenyline appears to have, if any, a very slight claim to the basic character.

The alcoholic solution of nitrosophenyline exhibits some remarkable optical properties. Perfectly transparent to transmitted light, it presents, when viewed in reflected light, a most extraordinary degree of opacity. A solution of 0·01 of a gramme dissolved in 5 grammes of alcohol, the solution thus containing only 0·2 of a per cent. of nitrosophenyline, exhibits this phenomenon in a very marked manner: a brilliant orange-red light illuminates the surface of the liquid, and descends to a slight depth beneath it; while the liquid itself appears as if finely

powdered vermilion were suspended in it. The flame of alcohol saturated with a baryta-salt is suitable for exhibiting the curious properties of this solution: but they are best seen when examined with the solar spectrum, the *red* ray producing no effect.

The colouring matter is acted upon by acids and by alkalies. The strongest hydrochloric acid and dilute nitric and sulphuric acids dissolve it with a magnificent crimson tint; ebullition with nitric acid produces a yellow colour; and solution in Nordhausen sulphuric acid, an intense brown, which nearly disappears on addition of water. Potash, soda, and ammonia partly precipitate the colouring matter from its acid solutions in brownish-yellow flakes; but if the action of the alkali be not prolonged, the original crimson tint of the solution reappears on the addition of an acid. From a solution of nitrosophenyline in hydrochloric acid, the colouring matter gradually separates as a reddish film, having the brilliant metallic lustre of copper. If nitrosophenyline be dissolved in the strongest hydrochloric acid, and the solution be exposed to the air, a gummy mass is formed after some time, while a portion of the nitrosophenyline separates: the hydrochloric acid in this compound does not exist in any definite proportion.

By the prolonged action of nascent hydrogen, nitrosophenyline loses its colorific properties, possibly passing into a substance containing no oxygen (and possessing the basic character?). The difficulty of preparing pure nitrosophenyline in sufficient quantity has prevented us from inquiring into the exact nature of this new product, but the inquiry would not be without interest. We have not as yet succeeded in regenerating from this colourless compound, by the action of oxidising agents, the original nitrosophenyline. All the analogues of nitrosophenyline which we have obtained suffer further reduction, producing colourless compounds by the prolonged action of hydrogen.

It was not surprising to find that dinitrobenzole is not the only substance of the benzole type from which a colouring matter may be produced in the way described. In the following table is a list of substances, homologous with dinitrobenzole, all of which give similar reactions with nascent hydrogen: —

1.	Dinitrobenzole	$C_{12}\,H_4\,2NO_4$
2.	Dinitrotoluole	$C_{14}\,H_6\,2NO_4$
3.	Dinitroxylole	$C_{16}\,H_8\,2NO_4$
4.	Dinitrocumole	$C_{18}\,H_{10}2NO_4$
5.	Dinitrocymole	$C_{20}\,H_{12}2NO_4$

The hydrocarbons from which the above-mentioned substances were produced had been obtained from very various sources. On account of the sparing solubility of *dinitroxylole*, &c., the compounds corresponding to nitrosophenyline in the higher terms of the series, are produced but sparingly by the method above given.

Composition of Nitrosophenyline.— Unlike most colouring matters, nitrosophenyline offers no difficulties in its analysis. In burning it, a stream of oxygen was employed towards the close of the combustion; in this way, the carbonaceous residue which it leaves on ignition was rapidly consumed. The nitrogen was determined by igniting the substance with soda-lime and precipitating the mixed hydrochlorates of aniline and ammonia with bichloride of platinum. As each equivalent of platinum corresponded to 1 eq. of nitrogen, the percentage of this latter element in the original substance was calculated from the amount of metal left on the ignition of the platinum-salts just mentioned. The following are the details of our analyses:—

I. 0·293 grm. of nitrosophenyline gave
0·634 „ „ carbonic acid, and
0·1235 „ „ water.

II. 0·2825 „ „ nitrosophenyline burnt with soda-lime gave
0·454 „ „ platinum.

In 100 parts:

	I.	II.
Carbon	59·04	
Hydrogen	4·68	
Nitrogen		22·80

These percentages lead to the formula

$$C_{12}H_6N_2O_2,$$

as may be seen in the following table:—

	Theory.		Experiment.
12 equiv. of carbon . .	72	59·01	59·04
6 „ „ hydrogen . .	6	4·92	4·68
2 „ „ nitrogen . .	28	22·95	22·80
2 „ „ oxygen . .	16	13·12	—
1 equiv. of nitrosophenyline .	122	100·00	

This formula is confirmed by the mode in which nitrosophenyline is formed from dinitrobenzole, $C_{12}H_4 2NO_4$, or from nitra-

niline, $C_{12} H_6 N_2 O_4$, and by the decompositions which it undergoes. As it forms no salts, the formula could not be controlled.

The relations of nitrosophenyline to dinitrobenzole and to nitraniline becomes simple and intelligible if we arrange the crude formula of nitrosophenyline as derived from the foregoing analyses, thus —

$$C_{12} \begin{matrix} H_4 \\ NO_2 \end{matrix}, NH_2;$$

or thus —

$$C_{12} \left(\begin{matrix} H_4 \\ NO_2 \end{matrix} \right) \Bigg\} N:$$
$$\begin{matrix} H \\ H \end{matrix} \Bigg\}$$

consequently, it differs from dinitrobenzole by containing 6 equiv. oxygen less, and 2 eq. hydrogen more; and from nitraniline by containing 2 eq. oxygen less. Thus, in the production of nitrosophenyline from dinitrobenzole, 1 eq. of NO_4 is replaced by 1 eq. NH_2, while the 2nd eq. loses 2 eq. of oxygen; the 1 eq. NO_4 in nitraniline is similarly reduced to NO_2. Nitrosophenyline may, in fact, be viewed as aniline in which 1 eq. of hydrogen is replaced by 1 eq. of NO_2; to such replacements Laurent has applied the terms "*substitutions nitrosées.*" From this expression we have constructed the name of the new colouring matter; but as this substance presents but a very equivocal basic character, we have preferred to call it nitrosophenyline rather than nitrosaniline. We are not without an example of a partial reduction of NO_4, somewhat similar to the present case. For, in the formation of azoxybenzole from nitrobenzole, we may imagine, with Laurent, that the reaction may be described in the following manner: —

$$\left.\begin{matrix} C_{12} H_5 NO_4 \\ C_{12} H_5 NO_4 \end{matrix}\right\} - 6O = \left\{\begin{matrix} C_{12} H_5 N \\ C_{12} H_5 NO_2. \end{matrix}\right.$$

2 eq. nitrobenzole — 1 eq. azoxybenzole.

The following list presents in a tabular form the derivation of nitrosophenyline, and the composition of those members of the benzole series which are related to it: —

1. Benzole $C_{12} H_5, H.$
2. Nitrobenzole $C_{12} H_5, NO_4.$
3. Dinitrobenzole $C_{12} \begin{matrix} H_4 \\ NO_4 \end{matrix}, NO_4 + 8H = C_{12} \begin{matrix} H_4 \\ NO_2 \end{matrix}, NH_2 + 6HO.$

4. Nitraniline $C_{12}\overset{H_4}{NO_4}, NH_2 + 2H = C_{12}\overset{H_4}{NO_2}, NH_2 + 2HO.$

5. Nitrosophenyline $C_{12}\overset{H_4}{NO_2}, NH_2.$

It is perhaps worthy of remark that nitrosophenyline presents considerable resemblance to the *red indigo* of Berzelius.

II. As we have said before, not only the homologues but the *analogues* of dinitrobenzole produce remarkable colouring matters when acted upon by nascent hydrogen. In order to ascertain the true nature of the new bodies thus produced, we have submitted to a detailed inquiry a beautiful red substance obtained by reducing *dinitro*-naphthaline with hydrogen. But a colouring matter perfectly identical may be procured by acting upon naphthalamine with nitrous acid, or upon the hydrochlorate of naphthalamine with nitrite of potash. By this last method we have obtained it in considerable quantities. This new substance resembles nitrosophenyline in its properties, and is perfectly analogous with it in composition, as we shall shortly show. We have termed it NITROSONAPHTHYLINE.

Properties of Nitrosonaphthyline.—When nitrite of potash is added to hydrochlorate of naphthalamine, nitrosonaphthyline is precipitated, nearly pure. It then merely requires washing with water, drying, and exhaustion with boiling spirits of wine. From this alcoholic solution, by slow evaporation in the water-bath, the colouring matter is gradually precipitated in minute crystals, very dark in colour, and having a green metallic lustre, similar to that of murexide. It imparts to alcohol a rich red tint, which is changed to a magnificent violet by acids, and restored to its original colour by alkalies. Water precipitates it from its alcoholic solution of a scarlet colour. Cotton, linen, paper, &c., may be permanently dyed of an orange tint by immersion in the alcoholic solution of nitrosonaphthyline. Materials so dyed, if plunged in acids, become of an intense purple hue, but in a stream of water the original orange tint speedily returns. Nitrosonaphthyline is insoluble in water. It may be fused without decomposition. Heated strongly, a portion sublimes unchanged; white fumes are afterwards given off, and a residue of carbon remains. Nitrosonaphthyline is not dissolved by dilute acids; strong nitric acid destroys it, but it is soluble in Nordhausen sulphuric acid, with a bluish-purple colour. Alkalies do not change the colour of

nitrosonaphthyline: but by the prolonged action of nascent hydrogen it is destroyed.

Composition of Nitrosonaphthyline.— The determinations of carbon, hydrogen, and nitrogen in this substance were made with the usual precautions, and gave the following numbers: —

I. 0·301 grm. of substance gave
0·77 „ „ carbonic acid, and
0·13 „ „ water.

II. 0·3205 „ „ substance burnt with soda-lime, gave
0·37 „ „ platinum.

These numbers correspond in 100 parts to

	I.	II.
Carbon . . .	69·76	—
Hydrogen . . .	4·80	—
Nitrogen . . .	—	16·39

These percentages lead to the formula

$$C_{20}H_8N_2O_2,$$

as may be seen by the following table: —

		Theory.		Experiment.
20 equiv. of carbon . . .		120	69·77	69·76
8 „ „		8	4·65	4·80
2 „ „		28	16·28	16·39
2 „ „		16	9·30	—
1 „ „ nitrosonaphthyline .		172	100·00	

Nitrosonaphthyline is quite analogous to nitrosophenyline: if the former be *aniline* in which 1 equiv. of hydrogen has been replaced by NO_2, the latter is naphthalamine, in which a similar substitution has taken place. The following equations sufficiently explain the various methods for the formation of nitrosonaphthyline: —

I. $C_{20}\overset{H_6}{NO_4}, NO_4 + 8H = C_{20}\overset{H_6}{NO_2}, NH_2 + 6HO$

II. $C_{20}H_7, NH_2 + NO_3 = C_{20}\overset{H_6}{NO_2}, NH_2 + HO.$

III. $C_{20}H_7, NH_2, HCl + KNO_4 = C_{20}\overset{H_6}{NO_2}, NH_2 + KCl + 2HO.$

A fourth method, which might be successful, suggests itself,

viz. the action of nascent hydrogen upon nitronaphthalamine. The reaction of aniline and NO_3 produces carbolic acid $C_{12}H_6O_2$, and not *nitrosophenyline*.

Nitrosonaphthyline dissolved in alcohol appears gradually to suffer partial decomposition. In the altered substance thus produced, the carbon amounts to 75 per cent.

The results of the present inquiry indicate the existence of an almost entirely new type of substitution-products,—bodies, too, remarkable alike for their physical properties and their chemical relations.

II. — *Action of Chloride of Cyanogen on Naphthalamine.*

By WILLIAM H. PERKIN.

MM. CAHOURS and CLOEZ, in their investigations on naphthalamine, observed that it combined with chloride of cyanogen, forming the hydrochlorate of a new base. They, however, did not investigate this subject any further; and as it was interesting to know whether compounds similar to those obtained from melaniline might be produced, I undertook, at the request of Dr. Hofmann, to examine this reaction more minutely.

Preparation of Naphthalamine. — The preparation of naphthalamine is effected by distilling nitronaphthaline with iron and acetic acid, according to the process of Zinin, modified by Béchamp.

This process yields the base in considerable quantity, but in an impure condition. To purify this, it must be dissolved in hydrochloric acid and water, and filtered from all insoluble impurities; the filtrate is then evaporated to dryness, and distilled with lime, when the base comes over nearly pure and perfectly anhydrous.

Preparation of Menaphthalamine. — In subjecting naphthalamine to the action of chloride of cyanogen, I adopted the same arrangement that Dr. Hofmann had used in the preparation of melaniline; namely, a series of tubes filled with the alkaloid through which the chloride of cyanogen was drawn by means of an aspirator. However, in this case it is necessary to support the action from the commencement by the application of heat, naphthalamine being a solid substance.

When the gas is passed into the fused anhydrous naphthalamine, chemical action is at once rendered perceptible by a rapid eleva-

tion of the temperature, and the gradual thickening of the liquid, which prevents the gas from passing freely. To complete the reaction, heat must be carefully applied sufficient to keep the compound in a state of fusion.

On cooling, the naphthalamine is found converted into a black resinous mass, which consists principally of the hydrochlorate of a base, which I propose to call menaphthalamine.

On boiling this mass in a large quantity of water, it almost entirely dissolves. On adding potassa or ammonia to the filtered liquid, a white precipitate is produced, which is freed from chloride of potassium, or ammonium, by washing with water, and recrystallised once or twice from alcohol, from which it is deposited in small white needles.

This base, when dried at 100° C. and burnt with protoxide of copper, gave the following numbers:—

I.	0·249	grm.	of menaphthalamine gave
	0·7385	„	carbonic acid,
	0·1275	„	water.
II.	0·2840	„	menaphthalamine gave
	0·8425	„	carbonic acid,
	0·1410	„	water.

These numbers lead to the following percentage composition:—

	I.	II.
Carbon . .	80·88	80·90
Hydrogen . .	5·40	5·50

Two analyses of the platinum-salt gave a mean of 19·065 per cent. of platinum.

Equivalent deduced from the platinum-salt	= 311·24
Theoretical equivalent	= 311·00

These results lead to the formula

$$C_{42}\,H_{17}\,N_3,$$

which require the following values:—

	Theory.		Mean of experiments.
42 equiv. of carbon. .	252·0	81·0	80·89
17 equiv. of hydrogen .	17·0	5·4	5·45
3 equiv. of nitrogen .	42·0	13·6	
	311·0	100·0	

This shows that the formation of menaphthalamine is perfectly analogous to that of melaniline and metoluidine, 2 equiv. of naphthalamine and 1 equiv. of chloride of cyanogen yielding 1 equiv. of the hydrochlorate of menaphthalamine.

$$\underbrace{2\,C_{20}\,H_9\,N}_{\text{Naphthalamine.}} + \underbrace{C_2\,N\,Cl}_{\text{Chloride of cyanogen.}} = \underbrace{C_{42}\,H_{17}\,N_3,H\,Cl}_{\text{Hydrochlorate of menaphthalamine.}}$$

Properties of Menaphthalamine. — This base, when pure, crystallises in small white needles, which are not coloured by exposure to the atmosphere.

Menaphthalamine is odourless; it has a bitter taste; fuses at about 200° C. into a transparent slightly yellowish oil. If the temperature be raised above 260° C., decomposition ensues, pure naphthalamine distils over, and a brown mass remains in the retort. In the case of melaniline, the residue had the formula $C_{54}\,H_{25}\,N_7$, which may be regarded as a compound of aniline-mellone with 3 equiv. of aniline.

$$C_6\,N_4\,(C_{12}\,H_4) = C_{18}\,H_4\,N_4$$
$$C_{54}\,H_{25}\,N_7 \quad = C_{18}\,H_4\,N_4 + 3\,C_{12}\,H_7\,N.$$

It is probable that the menaphthalamine residue has an analogous composition.

Menaphthalamine is almost insoluble in water, and only moderately soluble in alcohol and ether. It changes the colour of red litmus-paper. Chromic acid acts but slowly upon it.

COMBINATIONS OF MENAPHTHALAMINE.

This base forms salts with all acids, many of which are amorphous or very slightly crystalline. They are all sparingly soluble in water.

The salts have no action on litmus-paper. They are precipitated by acids and saline solutions; potassa and ammonia decompose them, the base being separated in the form of a pure white powder.

Hydrochlorate of Menaphthalamine. — This salt is a white amorphous compound, which becomes slightly red when exposed to air and moisture. It is moderately soluble in water, and very soluble in alcohol and ether: when heated, it is decomposed, hydrochlorate of naphthalamine subliming, and leaving a black residue in the retort.

A determination of hydrochloric acid gave the following result: —

0·4422 grm. of hydrochlorate gave
0·682 „ chloride of silver, corresponding to
10·44 per cent. of hydrochloric acid.

This number leads to the formula

$$C_{42}\ H_{17}\ N_3,\ H\ Cl,$$

which requires the following values: —

	Theory.		Experiment.
1 equivalent of menaphthalamine =	311·0	89·6	—
1 equivalent of hydrochloric acid =	36·5	10·4	10·44
	347·5	100·0	

Sulphate. — This salt is best obtained by neutralising sulphuric acid with menaphthalamine. It is a white, perfectly amorphous salt, moderately soluble in alcohol and ether, which on evaporation deposit it in the form of a white powder.

Nitrate. — This salt, which is the finest of all the menaphthalamine salts, may be prepared by adding menaphthalamine to very dilute boiling nitric acid. This solution, on standing, deposits the nitrate in small white prisms, nearly insoluble in cold water, but very soluble in alcohol and ether.

Phosphate. — It is a white crystalline salt, very soluble in alcohol and ether.

Binoxalate. — This salt is best obtained by boiling menaphthalamine with an excess of oxalic acid. From this solution the salt crystallises in small tufts of white needles, which are not easily soluble in water, but moderately soluble in alcohol and ether.

Hydrobromate and Hydriodate. — These salts are crystalline, and very soluble in alcohol.

Hydrochloroplatinate. — This compound is best prepared by adding an alcoholic solution of bichloride of platinum to a warm alcoholic solution of the hydrochlorate of menaphthalamine; from this solution, small yellow crystalline scales are deposited. If, however, the aqueous solutions are employed, it is immediately precipitated as an amorphous powder, which is almost white, but soon becomes slightly green.

Two determinations of the platinum gave the following numbers:—

I. 0·229 grm. of the salt gave
0·0435 „ „ platinum.

II. 0·19975 „ „ salt gave
0·03775 „ „ platinum.

	Theory.	Experiment. I.	Experiment. II.
Percentage of platinum in the platinum-salt . . .	19 08	19·04	19·09

Terchloride of gold gives with menaphthalamine-salts a blue precipitate.

METAMORPHOSES OF MENAPHTHALAMINE.

Menaphthalamine, when exposed to the action of various agents, undergoes a variety of transformations, many of which I have not been able to study.

Action of Sulphuric Acid. — When Nordhausen sulphuric acid is brought in contact with menaphthalamine, it becomes pasty, owing to the formation of the sulphate; but if a gentle heat be applied it becomes perfectly liquid. This liquid, on being diluted with water and treated with carbonate of lead, produces a soluble lead-salt, of a new acid, which decomposes partially every time it is evaporated.

On passing sulphuretted hydrogen through a solution of the lead-salt, a colourless solution is obtained (with precipitation of the lead as sulphide). When this liquid is evaporated, the new acid is decomposed into a soluble alkaline body, and an insoluble neutral one.

Action of Fuming Nitric Acid. — This acid acts violently on menaphthalamine, producing a variety of substitution-products.

Chlorine, bromine, and iodine seem to produce neutral compounds.

Action of Cyanogen. — If cyanogen is passed through an alcoholic or ethereal solution of menaphthalamine, it becomes first yellow, and then red, nothing being deposited on standing; but if the base is made into a thin paste with ether, and cyanogen passed through it, it all dissolves; and, on standing, the solution deposits a slightly crystalline body of a light buff colour, which may be purified by washing with ether.

A combustion of a specimen dried at 100° C. gave the following results:—

0·274 grm. of the substance gave
0·764 „ carbonic acid, and
0·1292 „ water,

which gives the following percentage composition:—

Carbon	76·00
Hydrogen	4·71

This may be translated into the formula

$$C_{46}\,H_{17}\,N_5,$$

as may be seen by the following table:—

	Theory.		Experiment.
46 equiv. of carbon . .	276	76·00	76·00
17 „ hydrogen .	17	4·69	4·71
5 „ nitrogen .	70	19·31	—
	363	100·00	

This compound, therefore, like dicyanomelaniline, is formed by the combination of two equivalents of cyanogen with one of menaphthalamine.

$$\underbrace{C_{42}\,H_{17}\,N_3}_{\text{Menaphthalamine.}} + \underbrace{2C_2\,N}_{\text{Cyanogen.}} = \underbrace{C_{46}\,H_{17}\,N_5}_{\text{New compound.}}$$

DICYMENAPHTHALAMINE (which name I propose for this compound) is a slightly buff-coloured body, which crystallises with difficulty; it is moderately soluble in alcohol and ether, but insoluble in water.

It is a base, though a very unstable one; it dissolves readily in dilute acids, and may be reprecipitated by ammonia if added directly after solution; but, like cyaniline and dicyanomelaniline, this base cannot remain in acid solutions without undergoing complete decomposition. If this base be dissolved in hydrochloric acid, and the solution allowed to stand for a few moments, it becomes cloudy, and a yellow substance begins to appear, which is not the hydrochlorate of dicymenaphthalamine.

The best process for the preparation of this new compound consists in adding dilute hydrochloric acid to a warm alcoholic solution of dicymenaphthalamine. On standing, it is deposited in

small scales of a yellow colour. The mother-liquors from the preparation of this compound always contained ammonia.

The analysis of this compound dried at 100° C. gave the following results:—

0·212 grm. of substance gave
0·590 „ carbonic acid, and
0·080 „ water.

These numbers lead to the following percentage composition:—

Carbon . . . . = 75·6
Hydrogen . . . . = 4·2

which may be translated into the formula

$$C_{46} H_{15} N_3 O_4,$$

as is evident from the following comparison of the theoretical with the experimental values:—

		Theory.		Experiment.
46 equiv. of carbon . .		276·0	75·66	75·6
15 „ hydrogen .		15·0	4·10	4·2
3 „ nitrogen .		42·0	11·50	—
4 „ oxygen . .		32·0	8·74	—
		365·0	100·00	

This substance, which I propose to call MENAPHTHOXIMIDE, is perfectly analogous in its properties to melanoximide.

Its formation is, as illustrated by the following equation,—

$$\underbrace{C_{46} H_{17} N_5}_{\text{Dicymenaphthalamine.}} + 4HO + 2HCl = \underbrace{C_{46} H_{15} N_3 O_4}_{\text{Menaphthoximide.}} + 2NH_4Cl.$$

This substance is insoluble in water, and very slightly in alcohol and ether, from which it may be crystallised, but with difficulty.

Menaphthoximide may be regarded as binoxalate of menaphthalamine minus 4 equivalents of water,—a view which is supported by experiment. On addition of potassa to this compound, menaphthalamine is reproduced, and the mother-liquor is found to contain oxalic acid.

The action of acids upon menaphthoximide is precisely the same as in the case of melanoximide; namely, it is converted into oxalic

acid, menaphthalamine, and a white neutral body, to which I intend to return at some future period.

Action of Heat on Menaphthoximide.—When menaphthoximide is heated to 245° C., it fuses; if the temperature be raised to 260° C., it decomposes, with evolution of a white vapour, having a most peculiar and powerful odour. I believe that this reaction is analogous to that which melanoximide undergoes when submitted to the influence of heat, and that the substance produced corresponds to Dr. Hofmann's anilocyanic acid,—in fact, that it is the naphthalamine term corresponding to cyanic acid, or naphthalocyanic acid; but I have not been able to obtain this compound in sufficient quantity to establish this supposition by experiment. I hope, however, to return to the examination of this most interesting subject as soon as possible.

In conclusion, I have to thank Dr. Hofmann for the advice and assistance he has afforded me during the prosecution of this investigation.

III.—*Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid.*

By Henry M. Noad, Ph.D.

LECTURER ON CHEMISTRY AT ST. GEORGE'S HOSPITAL.

In the Proceedings of the Royal Society, vol. viii. p. 532, there is an abstract of a paper "On Chemical Affinity, and the Solubility of Sulphate of Baryta in Acid Liquors," by Mr. F. Crace Calvert. The author says that "the insolubility of this salt is affected even by the weakest nitric or hydrochloric acids," and that "in future the practice of rendering liquors acid with either of these acids must be discontinued when sulphates are to be determined." In the abstract of Mr. Calvert's memoir, as it appears in the "Proceedings," the only experiments quoted relate to the solubility of sulphate of baryta in *nitric* acid; whether he extended his researches to hydrochloric acid, it is not stated; it is to be concluded that he did so, since, in a practical point of view, it is of far greater consequence to establish the fact, and the degree of the solubility of this sulphate in the latter acid than in

the former, the great majority of sulphur and of sulphuric acid determinations in mineral analyses being made in liquids containing excess of hydrochloric acid.

That sulphate of baryta is soluble to some extent in nitric acid, or at any rate that sulphuric acid may exist in nitric acid, both strong and dilute, and still no precipitate or even cloudiness be produced by the addition of a barytic salt, has, I believe, been known for some time to many chemists. Speaking for myself, I have certainly been aware of the fact for upwards of two years. I do not claim it as a discovery of my own, though I am quite unable to say from whom I derived my information. I have reason to believe, however, that the discovery originated with Mr. Nicholson, though the first public announcement of it is probably in Mr. Calvert's paper.

It is easy to prove that almost all the fuming nitric acid of commerce contains sulphuric acid, though it may retain a perfect transparency, when largely diluted with water, and treated with a barytic salt. All that is necessary is to evaporate an ounce or so of the acid, in a platinum capsule, down to about a drachm, then add water and nitrate or chloride of barium, upon which a greater or less turbidity will ensue. That very grave errors have been committed in sulphur determinations in organic compounds, in consequence of a want of the knowledge of this important fact, cannot be doubted, fuming nitric acid having been very generally employed as the oxidising agent to convert the sulphur into sulphuric acid: thousands of mineral analyses must, for the same reason, be considered erroneous as regards the determination of this particular element; and I consider myself fortunate that I was made aware of the almost invariable impurity of nitric acid, previous to the commencement of my own iron and cinder analyses, and thus have been enabled to guard against it. It is quite otherwise, however, as regards hydrochloric acid; and I must certainly confess that I read the abstract of Mr. Calvert's paper with considerable discomfort; for if his statement be true, then my own, and many thousand other sulphur determinations, have been made in vain, since in separating sulphur from phosphorus in crude iron and forge cinders I have almost invariably done so in an acid solution, and that acid has been *hydrochloric*. Being thus so immediately interested, and in the absence of all experimental evidence in the abstract of Mr. Calvert's paper, it was natural that I should forthwith commence a series of experiments to satisfy myself as to the justice or injustice of Mr. Calvert's con-

clusions; it being sufficiently evident that if the insolubility of sulphate of baryta is affected by the weakest hydrochloric acid, the usual course of mineral analyses must be somewhat modified. The results of my experiments I beg briefly to lay before the Society; they have proved the groundlessness of my fears, and may have the effect of relieving the minds of some other practical chemists as they have relieved mine. They show that though, under certain circumstances, the insolubility of sulphate of baryta is affected by weak hydrochloric acid, yet that the error likely to be thereby introduced into analysis is either altogether *nil*, or so exceedingly small as to be in most cases unworthy of consideration.

FIRST SERIES OF EXPERIMENTS.

Twelve liquors were prepared of uniform bulk,—the first consisted of 1000 grain measures of distilled water; the second of 900 grains of water + 100 grain measures of hydrochloric acid, sp. gr. 1153; the third of 800 grains of water + 200 grain measures of the same acid; the fourth of 700 grains water + 300 grain measures of acid; the fifth of 600 grains water + 400 grain measures of acid; the sixth of 500 grains water + 500 grain measures of acid; the seventh of 400 water + 600 acid; the eighth of 300 water + 700 acid; the ninth of 200 water + 800 acid; the tenth of 100 water + 900 acid; the eleventh of 1000 grain-measures of the acid without any water: 5 grains of neutral and thoroughly dried sulphate of potash were dissolved in each of these liquors; and, while boiling, solutions of 10 grains of nitrate of baryta in 300 grains of water were poured into each; they were allowed to remain at rest for twenty-four hours, then filtered, and the sulphate of baryta washed, dried, ignited, and weighed. In the twelfth experiment, the 5 grains of sulphate of potash were dissolved in 500 grain measures of hydrochloric acid, and the 10 grains of nitrate of baryta were boiled for some time with another 500 grain measures of the acid; little, if any, of the salt was dissolved, but abundance of chlorine was disengaged, and the liquor became dark yellow from the absorption of nitrous vapour. The acid liquor was decanted and added to the acid solution of the potash salt, sufficient boiling water was then added to dissolve the baryta-salt, and the liquors were then mixed, boiled, and the sulphate of baryta allowed to subside. The quantities of barytic sulphate obtained in the twelve experiments are given in the following table. The quantity of nitrate of baryta required theo-

retically to precipitate 5 grains of sulphate of potash is 7·5 grains, and the quantity of sulphate of baryta produced should be 6·70 grains.

Number of experiment.	Number of grain measures of water.	Number of grain measures of hydrochloric acid. Sp. gr. 1153.	Quantity of sulphate of potash used.	Quantity of nitrate of baryta used.	Quantity of sulphate of baryta produced.
1.	1000	0	5 grs.	10 grs.	6·74
2.	900	100	do.	do.	6·70
3.	800	200	do.	do.	6·71
4.	700	300	do.	do.	6·72
5.	600	400	do.	do.	6·69
6.	500	500	do.	do.	6·71
7.	400	600	do.	do.	6·78
8.	300	700	do.	do.	6·77
9.	200	800	do.	do.	6·76
10.	100	900	do.	do.	6·78
11.	0	1000	do.	do.	6·78
12.		500	do.	do.	6·78

It is seen that so far from there being a loss of sulphate of baryta, there is in the last six experiments a small apparent excess; this doubtless arose from a small portion of undecomposed nitrate having been carried down mechanically in the strongly acid liquor with the sulphate, from which it was not subsequently thoroughly removed by washing. It is well known that nitrate of baryta does adhere most pertinaciously to the sulphate when thus carried down, and requires long-continued washing to detach it; it is also well known that nitrate of baryta is very sparingly soluble in highly acid liquids. The precipitates were in all cases washed with the same quantity of boiling water, and the experiments show clearly, I think, that in this particular bulk of liquid, — viz. about 1000 grains measure, — the precipitation of sulphuric acid is complete in whatever proportion hydrochloric acid exists, — whether it forms the entire volume of the liquid, or whether it is absent altogether.

But Mr. Calvert says, "The solubility of sulphate of baryta is affected in a higher degree by the *bulk* of the acid than by its strength," and the table that he gives for nitric acid fully proves this to be the case. It became necessary to examine this position in relation to hydrochloric acid.

SECOND SERIES OF EXPERIMENTS.

5 grains of sulphate of potash were dissolved in 9000 grains of distilled water + 1000 grains of hydrochloric acid, sp. gr. 1153, and precipitated as before, while boiling, with a solution of 10 grains of nitrate of baryta. Three precisely similar experiments were made, and the following quantities of sulphate of baryta were obtained: —

I.	II.	III.
5·81	5·72	5·90

Mean . . 5·81 grs.

Here, then, there is a distinct loss of ·89 gr. of sulphate of baryta, but does this arise from a solution of the salt in the acid liquor, or is it the result of dilution? To determine this point, the same quantities of sulphate of potash were dissolved in the same bulks of acid and water, but double the quantity, viz. 20 grains of the precipitant, were employed: the proportions of sulphate of baryta now obtained in three experiments were—

I.	II.	III.
6 52	6·51	6·50

Mean . . 6·51 grs. Loss . . ·19 gr.

Three other solutions were then made and precipitated by 30 grs. of nitrate of baryta. The quantities of sulphate of baryta obtained were—

I.	II.	III.
6·71	6·69	6·71

the exact theoretical quantity. I must observe, that in these last six experiments the washings were continued for some hours, in order to avoid any possible error arising from the adhering of a portion of the precipitant to the precipitated salt.

By the side of these last experiments I placed two others, in one of which the 5 grains of sulphate of potash were dissolved in 10,000 grains of boiling distilled water, and in the other in

20,000 grains, no acid being added in either case: the quantities of sulphate of baryta obtained were —

I.	II.
6·73 grs. . . .	6·72 grs.

Lastly, the following experiment was made: —

5 grains of sulphate of potash were dissolved in a small quantity of water, and precipitated by 10 grains of nitrate of baryta; 10,000 grain measures of a mixture of 9 parts water and 1 part hydrochloric acid were then added, and the whole was boiled for 20 minutes; after 24 hours the resulting sulphate of baryta was weighed. Two precisely simila rexperiments were made, with the following results: —

I.	II.
4·4 grs. . . .	4·5 grs.

Here, then, was a loss of 2·3 grains of sulphate of baryta, one-third of the entire quantity that should have been obtained. The solubility of sulphate of baryta in a large bulk of dilute hydrochloric acid is proved conclusively by this experiment, but in a practical point of view it is not a matter of any importance; since, in the first place, it is not usual to attempt precipitations in such bulky liquids, but always to concentrate as far as possible; and, in the second place, it is always the practice to add considerable excess of the precipitant, which, as has been shown above, counteracts the tendency of the barytic sulphate to dissolve in the acid liquor. On the whole, then, I think that we may, without fear, continue to make our sulphur determinations in strong hydrochloric acid liquors, and that the only thing that the analyst has to guard against is the possible existence of sulphuric acid in the nitric acid he may employ as his oxidising agent.

While on the subject of sulphur determinations, I may allude to a method I have lately adopted for estimating the amount of this element in crude iron, which, with certain precautions, gives very accurate results, and which possesses the great advantage of enabling the operator to work upon much larger quantities of material than in any of the usual methods. The pounded iron is digested in a flask with dilute hydrochloric acid, and the gases evolved passed through three Wolfe's bottles, each containing a solution of arsenious acid; the whole of the sulphur of the metal passes over as sulphuretted hydrogen, and is estimated as As_2S_3. I have convinced myself, by repeated experiments, that the *whole* of

the sulphur is thus obtained in combination with the arsenic, and that the phosphorus which the crude iron invariably contains, though it is partly liberated, at the same time, in the form of phosphuretted hydrogen, does not interfere with the accuracy of the result. In what form the phosphorus combines with the arsenious acid, or whether it combines with it at all, I intend to make the subject of a special investigation; at present but little is known of the compounds of phosphorus with arsenic. I have, however, satisfied myself that no insoluble compound is formed under the circumstances of the above experiment. The only precautions to be observed are—1st, not to add too much hydrochloric acid to the water in which the arsenious acid is dissolved, the tersulphide not being so insoluble in hydrochloric acid as is generally supposed; nevertheless the solubility of arsenious acid in water is so greatly increased by the addition of a little hydrochloric acid, that a small quantity may be added with advantage; 2nd. the evolved gases must pass through at least three Wolfe's bottles, and it may occasionally be advisable to add a fourth; and, 3rdly, the connections between the bottles must be of *sheet* and not of *vulcanised* India rubber, it being almost impossible to keep the latter perfectly tight under the pressure to which they are subjected. I have occasionally employed solutions of nitrate and acetate of lead in the place of arsenious acid, but the objection to these salts is the great difficulty of washing thoroughly the bulky sulphide of lead: the results are, however, when carefully obtained, quite trustworthy.

IV.—*On the Source of the Water of the deep Wells in the Chalk under London.*

By Dugald Campbell.

The source of the supply of water to the deep wells in the chalk below London, is a subject which has occupied the attention of many persons, and has been discussed in several Societies on more than one occasion; but although this Society has recorded in its Journal the analysis of the water of several of the deep wells, still the origin of the source of their supply has not been considered much by the Society.

On this occasion I purpose to give, in as short a manner as I can, some of the views which have hitherto been maintained as to the origin or source of the water; and I shall endeavour to point out, from the results of my experiments upon the water, that its true source has not yet been suggested.

One of the theories most strenuously maintained, and apparently the most popular, is that the wells under London are partly supplied from the infiltration of sea-water, and partly from the infiltration of water from the chalk in the upper strata; and this view is supposed to be substantiated in a great measure by the chemical character of the water.

The advocates of this theory say that in the water of all the chalk-wells in or around London, which are below Trinity high water mark, the quantity of solid saline matter is very large, whereas, in the water of those wells which are above Trinity high water mark, there is comparatively a small quantity of solid saline matter. What they mean by solid saline matter are salts of potash and soda.

They take the water of the Trafalgar-square wells,—which, as far as my experience goes, contains the largest amount of solid saline matter of any water of the deep wells,—as a type of the water from below Trinity high water mark, and the water from wells at Watford in the upper chalk as a type of the water above Trinity high water mark.

They also say that the large amount of saline matter, together with the small amount of carbonate of lime or chalk, in the deep well-water,—just the opposite of what is found in the shallow chalk well-waters,—is another proof of the strong impregnation of the chalk-water with sea-water.

They likewise insist, that this view is considerably strengthened by the fact, that there is a gradual increase of the solid saline matter in the water of the London deep wells, which would not be the case were the water derived entirely from the upper strata, and had no supply whatever from the sea.

In order to show that the saline matter in the deep well-water is on the increase, Professor Brande's analysis of the Trafalgar-square water is quoted in comparison with Messrs. Abel and Rowney's analysis. According to Mr. Brande, in 1846 the solid contents per gallon were 66·1 grains, consisting of 59·9 grains of soda salts and 3·1 grains of carbonate of lime, with 2·4 grains of carbonate of magnesia; by Messrs. Abel and Rowney's analysis, in 1849 the solid contents per gallon were 68·24 grains,—showing an increase on the whole of 2·14 grains of solid matter per gallon;

and "this increase was principally due to salts derivable from sea-water, there being only 0·17 grain increase in the carbonate of lime."

I may just mention, that in Mr. Brande's analysis no volatilised or organic matter is given; and were this supplied, I believe there would be little difference in the amounts of solid contents in the two analyses; indeed, were the organic matter estimated by the method generally employed at that time, and still I believe retained by many analysts, it would amount to more than 2·14 grs.,—the excess of solid contents found by Messrs. Abel and Rowney over that found by Mr. Brande. This method of estimating the organic matter in water, to which I have alluded, was to evaporate a portion to dryness, weigh the residue, and afterwards heat it to low redness till it ceased to lose weight, when the difference from its former weight would be considered the organic matter.

In 1850, my attention was directed to the Trafalgar-square water, and I then found that the solid contents, including organic matter, were per gallon 61·60 grains, or 6·64 grains per gallon less than when it was examined by Messrs. Abel and Rowney in 1849.

In the Society of Civil Engineers, last July, it was again stated that the salts were increasing in the water of the Trafalgar-square deep wells, and I then directed my attention to the subject, procured specimens of the water, and made an analysis of it, when I found that what had been stated was not the case, and the saline contents were less than when I examined it in 1850.

Perhaps I may be allowed a digression here to state that, before this, I had analysed the water from many of the deep wells in different parts of London, and in all I had found a large amount of soda-salts, and a small though weighable quantity of potash-salts, varying in potash from 0·327 grain in a gallon to as much as 1·33 grain; but I was scarcely prepared to find the Trafalgar-square water to have the same character, Messrs. Abel and Rowney having found 13·67 grains of sulphate of potash in a gallon;* however, on procuring a copy of the minutes of the Proceedings of the Civil Engineers, vol. ix., I for the first time saw Mr. Brande's analysis, and either he had not detected any potash-salts in the water, or they were in such small quantities as not to be considered by him worth noticing, for they are not given in the analysis.

* Chem. Soc. Qu. J. i. 97, *et seq.*

I have placed in a table my analysis of the Trafalgar-square well-water, together with an analysis of the Watford chalk-water, and also an analysis by Dr. Schweitzer of the water of the English Channel; so that at one glance a comparison of their composition may readily be made, in order the better to test the different views which have been set forth as to the source of the supply of the deep well-water in the chalk under London.

TABLE OF ANALYSES.

Substances found.	Trafalgar-sq. water, grs. in a gallon at 60° Fah.	Watford water, grs. in a gallon at 60° Fah.	Eng. Channel sea-water, grains in a gallon.
Carbonate of soda -	10·58		
Sulphate of soda -	21·34	0·70	
Chloride of sodium -	19·04	1·39	1894·13
Carbonate of potash -	1·05		
Chloride of potassium -			53·55
Carbonate of magnesia	2·07		
Sulphate of magnesia -			160·65
Chloride of magnesium			256·62
Bromide of magnesium			2·03
Carbonate of lime -	2·74	18·20	2·31
Sulphate of lime -			98·42
Nitrate of lime - -		1·76	
Phosphate of iron and lime - - -	0·97		
Silica - - -	0·40	0·81	
Volatilised matter -	0·66	0·81	
Total - -	58·85	23·67	2467·71

In the analysis, I have combined the acids with the bases, but not before getting as good an insight into the constitution of the water as can be obtained, by taking its degree of hardness and alkalinity before, and likewise after submitting it to the softening process of Dr. Clark.

I may observe, that the volatile or organic matter is obtained as follows: — The water is evaporated to dryness in a platinum

capsule, and the solid contents dried until they cease to lose weight at the temperature of 260° Fah.; the weight is then noted, and the capsule heated to low redness until no more loss of weight takes place; the contents are then saturated with fresh carbonic acid water, and dried at 260°; and this operation of saturating with carbonic acid water and drying is repeated until an uniform weight is obtained: the difference between this and the first weight before heating to low redness, is volatilised or organic matter. This is not an exact method of estimating volatile or organic matter, there being none; still I think it is the most correct known; for if the residues, after evaporating the water, are simply heated to redness and weighed, no two results are obtained alike from the same water. The process given is better in this respect: besides, the water originally is not caustic, whilst a solution of the residue in water which has been heated to redness generally is, — indicating that it has been deprived of acid. In the residues from water, I find carbonic, nitric, and even sulphuric acid, affected by the heating to redness. Restoring the carbonate as described was suggested by Dr. Clark.

The results which I obtained, as I stated before, show that the salts in the water have decreased, since 1850, 2·75 grs. per gallon, and since 1846 altogether 9·39 grs. per gallon, — a result rather fatal to the statement that the salts are increasing in the water, and also to the idea of a percolation of sea-water into the wells.

But I think it is only necessary to compare an analysis of the deep well-water with that of a proper chalk-water, together with an analysis of sea-water, as in the table I have given, to be convinced that the deep well-water is no mixture of chalk and sea-water; and it is quite clear, without making an experiment, that under no circumstances could a mixture of sea-water with chalk-water in any proportion produce the deep well-water. To account for the presence of carbonate and sulphate of soda alone in the deep well-water, without going further into the matter, is impossible.

As a modification of the first view given, it has been suggested that the water may still be a mixture of chalk-water and sea-water, only the sea-water has undergone a change by percolating through the chalk strata before reaching the wells. There can be no doubt that the first portions of sea-water passing through chalk would be deprived of their salt to a great extent, if not entirely; but as the chalk became saturated with sea-water, the water would, in passing through, increase in its saline properties, and in time

would become sea-water. But this, I have shown, is not the case: besides, the analysis of the three waters will not admit of this view; for common salt is not decomposed in an ordinary way by carbonate of lime or sulphate of lime. But granting for a moment, for the sake of argument, that, by some means which we know not of, it underwent decomposition, still the chlorine which was originally combined with the decomposed chloride of sodium —and it is not a small quantity—is not to be traced in the analysis of the deep well-water, but has entirely disappeared out of it,—a thing I would consider chemically impossible.

An observation I have made, and which I do not think has been noticed before by anyone writing upon the subject, is, that the deeper wells in the chalk contain more saline matter in a gallon than the shallow ones,—rather a strong fact, I consider, against the view of the infiltration of sea-water into the wells, for sea-water should become less saline in proportion to the thickness of chalk it has to percolate through, and not more saline.

Another view of the source of the deep well-water, which has been supported by no mean chemical authority, is, that it is ordinary chalk-water which has been decomposed by percolating through the chalk strata, and has no sea-water in its composition.

The explanation given of how it is changed is as follows:—Silicate of soda is found in the chalk through which the water percolates; this silicate is decomposed by the carbonate of lime in the water, insoluble silicate of lime deposits, and the carbonate of soda gets into solution in its place.

This may be very well to account for the increase of the carbonate of soda, and decrease of carbonate of lime in the deep well-water, but it does not in any way afford a solution for the presence of chloride of sodium and sulphate of soda in such large quantities as these salts are found in the deep well-water.

My own conviction is, that the water does not originally come from an ordinary chalk stratum; indeed, I believe that the deep wells have a separate and independent source, and are not supplied from the upper chalk-water at all. This view has been strengthened by my having observed a peculiarity in the water of the deep wells not hitherto, I think, noticed,—namely, that there is scarcely the slightest, if any, indication of nitrates in the proper deep well-water; whereas all waters from the upper chalk which I have examined, and these are not a few, contain a notable quantity of nitrates,—indeed, it is a characteristic of a proper chalk-water to do so. The Watford water, one of the purest chalk-waters to be

met with, gave on an average of several examinations 1·76 grain of nitrates per gallon, as noted in the table.

As the deep well-water contains phosphates (an observation which was made by Mr. Graham*), and as phosphates are generally associated with animal or vegetable substances, I should have expected an increase of nitrates in this water over the ordinary chalk-water, from the oxidation of nitrogenous matter accompanying the phosphates; but the freedom from nitrates, especially under the circumstances, is certainly very peculiar, and the inferences to be drawn from it are, that either the phosphates in the water are not originally derived from an organic source, or, if they are, that large quantities of water must have passed through the strata in which these organic remains were deposited, and thus have washed away the more soluble nitrates from amongst them. This, I believe, is really what has taken place.

Before forming an opinion myself of the source of the deep well-water in the chalk, I thought it was necessary to examine, if possible, the water from the different strata which form the London Basin; and for this purpose I procured what I was told was a specimen of water from the plastic clay or tertiary strata, and from that part of the strata which immediately overlies the chalk. I did not make a full analysis, but only estimated certain substances in it; my results, however, showed this water to have a great similarity in many respects to the deep well-water, but they differed so much from analyses already published upon the water, that I thought perhaps I might not have had a genuine specimen given to me; and as it is a point too intimately connected with this subject to be entirely passed over, I deferred proceeding further until I had a little more leisure, and until I could procure and examine other specimens, and, if possible, from wells in the strata in different localities, when I hope, with the kind permission of the Society, again to bring the subject before their notice.

* Chem. Soc. Mem. ii. 392.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 21, 1856.

The MASTER of the MINT, Vice-President, in the Chair.

The following donations were announced:—

"The Journal of the Society of Arts:" from the Society.
"The Journal of the Photographic Society:" from the Society.
"The Literary Gazette:" from the Publishers.
"The Pharmaceutical Journal:" from the Editor.
"The Journal of the Franklin Institute:" from the Institute.
"The American Journal of Science and Art:" from the Editors.
"On the Action of Water upon certain Sulphomethylates:" by A. H. Church. From the Author.
"On the Spontaneous Decomposition of certain Sulphomethylates:" by A. H. Church. From the Author.

Dr. H. E. Roscoe was elected a Fellow of the Society.

Dr. W. A. Miller delivered a discourse "On some points in the practice of the Assay of Gold and Silver."

February 4, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"Elements of Chemistry, Theoretical and Practical," Second Part: by Dr. W. A. Miller. From the Author.
"Report of the Commission appointed to make Inquiries into

the state of the Manufacture of Iron and Brass Ordnance:" from F. A. Abel.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Photographic Society:" from the Society.

"The Literary Gazette:" from the Publishers.

"The Pharmaceutical Journal:" from the Editor.

"The Memoirs and Proceedings of the Academy of Sciences of Madrid, for the years 1851, 1852, and 1853:" from the Academy.

The following papers were read:—

"Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre:" by F. A. Abel and C. L. Bloxam.

"Note on the Solubility of Sulphate of Baryta in Hydrochloric Acid:" by Henry M. Noad, Ph.D.

Dr. A. W. Hofmann made a verbal communication "On a New Class of Alcohols."

February 18, 1856.

Dr. W. A. Miller, President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Franklin Institute:" from the Institute.

"The Report of the Council of the Art-Union of London for 1856:" from the Art-Union.

"The Almanack of the Art-Union of London for 1856:" from the Art-Union.

"On the supposed Influence of the Hot-Blast in augmenting the quantity of Phosphorus in Pig-Iron:" by David S. Price, Ph.D., and Edward Chambers Nicholson. From the Authors.

Nathan Mercer, Esq., of Liverpool, was elected a Fellow of the Society.

Dr. A. W. Hofmann delivered a discourse "On some New Bases containing Phosphorus."

March 3, 1856.

Dr. A. W. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.
"The Journal of the Photographic Society:" from the Society.
"The Journal of the Society of Arts:" from the Society.
"The Pharmaceutical Journal:" from the Editor.

The following gentlemen were elected Fellows of the Society:—

G. C. Foster, B.A., University College, London.
Arthur Herbert Church, Esq., 9, Bedford Row, Gray's Inn.
Augustus Beauchamp Northcote, Esq., 37, Argyle Square.

The following papers were read:—

"On the Source of the Water of the deep Wells in the Chalk under London:" by Dugald Campbell.
"On the Action of Chloride of Cyanogen on Naphthalamine:" by William H. Perkin.
"On some New Colouring Matters, Derivatives of Dinitrobenzole, Dinitronaphthaline, &c.:" by A. H. Church and W. H. Perkin.

March 17, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"The Journal of the Franklin Institute:" from the Institute.
"Bericht der kaiserlichen Akademie der Wissenschaften zu Wien:" from the Academy.

Dr. J. H. Gladstone delivered a discourse "On some Laws of Chemical Combination."

ANNIVERSARY MEETING,

March 31, 1856.

Dr. W. A. MILLER, President, in the Chair.

The Report of the Council, and the Audited Account of the Treasurer, were read.

It was Resolved,—

"That in By-Law 2, 'Of Honorary and Foreign Members,' the first sentence of the second paragraph be altered, and in future stand as follows:—'The number of Foreign Members shall not exceed twenty-five.'"

Mr. W. Ferguson and Mr. A. B. Northcote having been appointed Scrutators, the meeting proceeded to the election of Council and Officers for the ensuing year, and the following gentlemen were declared to have been duly elected:—

PRESIDENT.

W. A. Miller, M.D., F.R.S.

VICE-PRESIDENTS
(WHO HAVE FILLED THE OFFICE OF PRESIDENT).

W. T. Brande, F.R.S.
C. G. B. Daubeny, M.D., F.R.S.
Thomas Graham, F.R.S.
Colonel Philip Yorke, F.R.S.

VICE-PRESIDENTS.

B. C. Brodie, F.R.S.
Warren De la Rue, Ph.D., F.R.S.
G. D. Longstaff, M.D.
A. W. Williamson, Ph.D., F.R.S.

SECRETARIES.

Theophilus Redwood, Ph.D.
William Odling, M.B.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.R.S.

TREASURER.

Robert Porrett, F.R.S.

OTHER MEMBERS OF THE COUNCIL.

F. A. Abel, Esq.
C. L. Bloxam, Esq.
G. B. Buckton, Esq.
Dugald Campbell, Esq.
J. H. Gilbert, Ph.D.
W. C. Henry, M.D., F.R.S.
William Herapath, Esq.
Charles Heisch, Esq.
H. Bence Jones, M.D., F.R.S.
Hugh Lee Pattinson, F.R.S.
John Stenhouse, LL.D., F.R.S.
John Thomas Way, Esq.

It was moved by Dr. A. W. Williamson, seconded by Robert Porrett, Esq., and Resolved,—

"That Professor Benjamin Collins Brodie having resigned the office of Secretary, this meeting desires to express their regret at the loss of his services, and request the President to convey to him, in the form he may think most suitable, their thanks for the zeal he has manifested in promoting the interests of the Chemical Society; and, at the same time, to congratulate him on the more extensive sphere of action to which he has lately been appointed."

The thanks of the meeting were voted to the President, Officers, and Council, for their services during the past year.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

Chemical Report on the Mode of Detecting Vegetable Substances mixed with Coffee for the purpose of Adulteration.

By T. Graham, F.R.S., J. Stenhouse, F.R.S., and D. Campbell, F.C.S.

THE adulteration of coffee in the condition of the original bean, unground and unroasted, could only be effected by the substitution of a different seed, and would form the subject of an inquiry entirely botanical. But it is proper to remark that the coffee-bean is liable to be rendered entirely worthless, without any injury to its structure, when kept in a wet or damp state for some time,—apparently from the readiness with which the soluble constituents of the bean spontaneously ferment. Coffee damaged by sea-water has been found to retain neither the aroma nor bitter flavour of the seed, and to have lost the whole of its characteristic principle, caffeine. The entire soluble matter which can be extracted from the damaged seeds by boiling water is greatly reduced, and does not exceed 12 per cent. of their weight, while the presence of the salts of sea-water is always sufficiently obvious.

The coffee-bean, in its fresh, unprepared state, is tough, and ground with difficulty. It yields an infusion without aroma, which is bitter, and is said to act more powerfully on the nerves than roasted coffee. This seed, however, is always roasted before being made use of, and it is in that state, and with its structure more or less obliterated by grinding, that it must be identified, and its purity established by chemical means of investigation.

In consequence of torrefaction, coffee is materially altered, and acquires new properties. The woody tissue of the fresh bean is

horny, and differs from ordinary woody fibre in its composition, and is also said not to yield sugar when treated with sulphuric acid. By the roasting, this woody tissue undergoes a partial decomposition, and becomes friable, and the difficulty of pulverising the seed, and exhausting it by water, is removed. There is produced at the same time a soluble brown bitter matter, due in part to a gummy substance pre-existing in the coffee, altered like starch by torrefaction, but principally to the conversion into caramel of a quantity of sugar in the coffee-bean, amounting to 6 or 7 per cent. of its weight.

A still more characteristic product of the roasting of coffee, is that which gives it aroma. This principle, when separated from the infusion of coffee by distillation, is found to be a brown liquid oil, heavier than water, soluble in ether, and has received the name of *Caffeone* (Boutron and Frémy). Caffeone is slightly soluble in boiling water; a quantity of caffeone which is almost insensible will aromatise two or three pints of water.

In common with all the valuable constituents of coffee, caffeone is found to come from the soluble portion of the roasted seed.

The caffeic acid of the green coffee is also changed by the roasting into an acid of different properties.

Of the crystallisable caffeine, a small portion may be lost from its volatility in roasting.

No seed appears to be known, which, roasted and pulverised, forms a true equivalent and sufficient substitute for coffee, either in the physiological properties or chemical composition of its soluble extract. A great variety of seeds were tried in France, as substitutes for coffee, during the continuance of the Continental blockade, including, in addition to maize, barley, oats, and the other cereals, the seeds of the yellow flag (*Iris pseudo-acorus*), grey pea (*Cicer arietinum*), the milk vetch, or Andalusian astragalus (*Astragalus boeticus*), the *Hibiscus esculentus*, holly, Spanish broom, acorns, chesnuts, the small lupin (*Lupinus angustifolia*), peas, haricots, horse-beans, sunflower, pips of the gooseberry and grape, eglantine (*Rosa villosa*), and the capsules of box (*Buxus sempervirens*). Of the seeds enumerated, the yellow flag, a common marsh plant in England, appears to have offered the only similarity to coffee; but it is doubtful whether the resemblance extended beyond the aroma of this seed when roasted, which is certainly suggestive of coffee.

The search made among the seeds of other plants for a substitute for the coffee-berry may then be said to have entirely failed.

The divergence of the root-substitutes from true coffee is still greater in every property except one. The roots which have been most used are those of chicory (*Cichorium intybus*), carrot,

beet, rush-nut (*Cyperus esculentus*), earth-nut (*Arachis hypogæa*), scratch-weed (*Gallium aparine*), fern (*Polypodium filix mas*), and butchers' broom (*Ruscus aculeatus*).

The roots of chicory, and of beet and carrot, which are all extensively used in Germany, are similarly prepared, being cut into thin slices, dried in a stove, and then passed through a coffee-roaster,—generally with the addition of about 2 per cent. of butter, and sometimes of a red powder, to give the colour of coffee.

It is to be remarked of the roots, that they are generally used rather as an addition to coffee than as a substitute for it. In one property these roots all agree, and we have no doubt that it has led to this common application of them: chicory, beet, carrot, &c., are all remarkable for containing a large quantity of sugar, easily caramelised by heat. They acquire, when roasted, the bitter of burnt sugar, with a somewhat similar aroma. Now the taste of this bitter appears to be one of the strongest and most general of our gustatory preferences. It equally recommends toast-water, and the varieties of brown beer or porter, in the preparation of which a portion of malt is used with its sugar caramelised by heat. The caramel bitter is, in fact, a stock flavour, which we find modified by the most various accessories in different beverages, and even in solid articles of diet in a cooked state. It is not surprising, therefore, that the chicory root, containing as it does about 30 per cent. of sugar, more than one-half of which is caramelised in roasting, should obtain extensive favour as an addition to coffee. Fresh chicory has a certain bitterness, or rather acridity, but this is overpowered in the torrefied root by the caramel bitter, and this root may be adequately replaced by the bland beet or carrot similarly prepared. No one of these roots contains any constituent which associates it with coffee, except sugar:—in other respects they are entirely different.

The preparation of roasted chicory appears to have originated in Holland upwards of a century ago, but remained secret till 1801. It is now prepared on a great scale, both on the Continent and in England. The quantity of chicory-powder consumed annually in France is known to amount 6,000,000 kilogrammes.

In the chemical examination of ground coffee, with the view to discover if it is mixed with the vegetable substances which have been named, or with others, the characteristic constituents of the coffee are less immediately available than certain properties of the infusion of a physical character. This arises from the circumstance, that although it is easy to discover the presence of caffeic acid and caffeine, yet the determination of the exact quantity of these substances in an infusion is both difficult and tedious.

There is reason also to believe that the proportion of caffeic acid

and caffeine varies considerably in different samples of coffee, so that the quantities of these substances (when found) could not show exactly the proportion of pure coffee in a mixture. It will be most advantageous to discuss here the general properties of the coffee infusion, in the first instance, as they are most easily observed; and a single character of this kind in some instances, and two or three in others, will generally be sufficient to establish adulteration when it has been practised. The higher chemical inquiries will then follow.

1. When hot water is applied to the powder of chicory and other roots, it softens immediately, from the facility with which water is imbibed, while the grains of coffee remain hard and gritty in the same circumstances. Ground chicory is highly hygroscopic.

Roasted grain, such as wheat and barley, gives an infusion with hot water, which is mucilaginous and thick, while the infusion of coffee is remarkably thin and limpid. The grain infusion generally contains starch, and gives, when cool, a blue colouration with iodine, while the infusions of both coffee and chicory appear to be entirely destitute of starch.

2. The more deep and rapid coloration of water by chicory and the allied roots than by coffee, affords a useful indication in a preliminary examination. The roasted grains also appear to colour water more deeply than coffee does. The relative colouring power of coffee, chicory, and a variety of other vegetable substances used in the adulteration of coffee, was determined with considerable precision by infusing equal quantities of each in water, as in the preparation of coffee, filtering the infusions through paper, and observing the colour in glass tubes of equal diameter—about 1 inch. The solutions required to be very dilute. It was also necessary to have a standard of comparison, and for this purpose caramel, carefully prepared from cane-sugar, was had recourse to. The standard solution of caramel consisted of 1 grain of that substance dissolved in 2000 grains of water. To produce the same intensity of colour as the standard solution, a larger proportion than 1 grain of all the other substances required to be dissolved in 2000 grains of water. The proportion necessary is expressed in Table I. The substances are all roasted, as they would be used to mix with coffee.

Table I.

Weight of substance (roasted) dissolved in 2000 parts of water, to produce an equal depth of colour.

Caramel	1·
Mangold-wurzel	1·66
Bouka (a coffee substitute)	1·66
Sparke's vinegar colouring	1·74
Black malt	1·82
White turnips	2·0
Carrots	2·0
Chicory (darkest Yorkshire)	2·22
Parsnips	2·5
Maize	2·86
Rye	2·86
Dandelion root	3·33
Red beet	3·33
Bread raspings	3·64
Acorns	5·00
Over-roasted coffee	5·46
Highly-roasted coffee	5·77
Medium-roasted coffee	6·95
Another specimen of coffee	6·66
White lupin seed	10·00
Peas	13·33
Beans	13·33
Spent tan	33·
Brown malt	40·

It will be seen from the preceding table, that 2·22 parts of chicory have the same colouring power as 5·77 grains of highly-roasted, and 6·95 grains of medium-roasted coffee, or of 13·33 grains of roasted peas, and 40 parts of brown malt.

The same results are given in a different form in Table II.

Table II.

Colouring power of various substances (roasted) dissolved in an equal quantity of water.

Caramel	1000·
Mangold-wurzel	602·4
Bouka (a coffee substitute)	602·4
Sparke's vinegar colouring	574·71
Black malt	549·45
White turnips	500·
Carrots	500·
Chicory (darkest Yorkshire)	450·45

Parsnips	400·
Maize	350·
Rye	350·
Dandelion root	300·3
Red beet	300·3
Bread raspings	274·72
Acorns	200·
Over-roasted coffee	183·15
Highly-roasted coffee	173·31
Medium-roasted coffee	143·88
Another specimen of coffee	150·15
White lupin seed	100·
Peas	73·18
Beans	75·18
Spent tan	30·
Brown malt	25·

The number for chicory (450) indicates that that substance possesses nearly half the colouring power of caramel (1000); while highly-roasted coffee (173) is about one-sixth of caramel. Maize and rye, with probably all the other cereals, rise to 350, and have therefore a high colouring power, quite double that of coffee; while peas and beans (75) are on the other side, and possess only about half the colouring power of coffee for equal weights of the substances compared.

The preceding solutions were prepared at 212°, and chicory then exhibits about three times the colouring power of coffee. But when the solutions are prepared without heat, the disparity is still greater. In cold water chicory exceeded coffee about four and a half times in colouring power.

When a few grains of roasted chicory, or any other sweet root, are dropped into a glass of cold water, without being stirred, a yellowish-brown colour diffuses rapidly through the liquid, while the pure coffee gives no sensible colour to the water in similar circumstances.

3. Another property of infusions, which is still more precise and valuable, is their specific gravity.

The proportion of substance found most suitable for an extensive comparison was 1 in 10 of water. The substances were not exhausted by water, but simply placed in about a pint of cold water, in the preceding proportion by weight, and the temperature raised to 212°, and retained at that point for not more than half a minute. The infusions were then filtered through paper. The substances, as usual, are roasted and ground equally fine, with the exception of the last three in the table.

Table III.

Specific gravity of solutions at 60° F., 1 part of substance to 10 parts of water.

Spent tan	1002·14
Lupin seed	1005·7
Acorns	1007·3
Peas	1007·3
Mocha coffee	1008·0
Beans	1008·4
Neilgherry coffee	1008·4
Plantation Ceylon coffee	1008·7
Java coffee	1008·7
Jamaica coffee	1008·7
Costa Rica coffee	1008·98
Native Ceylon coffee	1009·0
Costa Rica coffee	1009·5
Brown malt	1010·9
Parsnips	1014·3
Carrots	1017·1
Bouka	1018·5
English chicory (Yorkshire)	1019·1
Black malt	1021·2
Turnips	1021·4
Rye meal	1021·6
English chicory	1021·7
Dandelion root	1021·9
Red beet	1022·1
Foreign chicory	1022·6
Guernsey chicory	1023·2
Mangold-wurzel	1023·5
Maize	1025·3
Bread raspings	1026·3
British gum	1037·9
Gum arabic	1038·6
Cane sugar	1040·9
Starch sugar	1042·8

The leguminous seeds, it appears, give a low specific gravity,—peas 1007·3, and beans 1008·4. The coffees are also remarkably low, varying from Mocha coffee 1008·0, to Costa Rica 1009·5; while chicory rises greatly, ranging in different samples between 1019·1 and 1023·2. The cereals are equally high, or still higher, in the scale of gravity; rye-meal being 1021·6, and maize 1025·3. The low gravity of the coffee infusion, therefore, distinguishes it sharply from the two most important classes of adulterating substances,—the roots and cereals.

4. The action of other solvents, besides water, may be shortly referred to.

Agitated four times successively in ten times their weight of ether, the substances to be mentioned gave different proportions of matter soluble in that menstruum:—

Roasted beans .	.	.	1·81	per cent. of oil and resin,
„ maize .	.	.	5·15	„ „ „
„ chicory (Yorkshire)			6·83	„ „ „
„ coffee (Mocha)	.		15·93	„ „ „

including probably nearly 1 per cent. of caffeine.

It thus appears that coffee yields much more soluble matter to ether than beans, maize, or chicory, which represent the three classes of leguminous seeds, cereals, and sweet roots. The fat obtained from chicory was no doubt principally composed of the sweet American or Australian tallow, added by English manufacturers to the root, in roasting, to prevent burning. The experiment with ether is easily made, and may in particular circumstances prove valuable.

The solubility of the same substances in proof spirit was observed, the substance being exhausted four times in succession by ten times its weight of proof spirit, at the boiling temperature.

Roasted beans gave 17·5 per cent. of a dry, blackish, lustrous extract.

Roasted maize gave 50·2 per cent. of an extract much like the preceding.

Roasted chicory (Yorkshire) gave 67·76 per cent. of extract of a lighter colour than the preceding, but otherwise very similar.

Roasted coffee (Mocha) gave 26·35 per cent. of extract, much like the first two in external appearance.

These operations are remarkably tedious, while the experiments with ether, on the contrary, are easy and simple. The results with proof spirit are not sufficiently characteristic to recommend its application.

5. Fermentation by means of yeast gives a decisive proof of the adulteration of coffee by many vegetable substances, particularly by chicory and the other saccharine roots.

In our fermentation experiments, 2000 grains of the coffee or other substances were weighed out, and treated successively with $1\frac{1}{2}$ pint of cold water, $1\frac{1}{2}$ pint of water about 174°, and a little additional water for washing the solid residue upon a filter of fine calico. About 3 pints of infusion were thus obtained, which were mixed with 250 grains of brewers' yeast, weighed after being pressed in a calico bag. The fermentation was continued for forty-eight hours at a temperature of from 80° to 90°. The fermented liquor was afterwards distilled, and about 6000 grains

brought over. The last vinous liquor was rectified a second time, about 3000 grains being now collected; and the alcohol was inferred from the density of this distillate.

The substances were examined for sugar both before and after being roasted, as it was interesting to observe the extent to which the sugar is caramelised, by torrefaction, in the different substances.

The sugar of coffee is found to be reduced by roasting from 6 to 7 per cent. in raw coffee, to from 0· to 1·12 per cent. in the roasted,—or to be almost entirely destroyed; while in other substances the sugar is more generally reduced, by precisely similar treatment, to from one-half to one-third of its original proportion. It is difficult to account for this dissimilarity, unless a portion of the sugar of raw coffee exists in a state of conjugate combination, like the sugar in tannin, amygdalin, salicin, &c.: our attempts to isolate such a conjugate body, however, from raw coffee, have not yet proved successful, and its existence is therefore hypothetical. We succeeded, on the other hand, in crystallising out cane-sugar from an infusion of raw coffee. It was decided by proper experiments that the fermentation of sugar was not interfered with by the empyreumatic products, or essential oil of roasted coffee.

The sugar was determined which exists in the most dissimilar varieties of coffee, the wild and cultivated beans, the beans from Ceylon and the West Indies, from Arabia, and the Neilgherry Hills. Twelve different samples were examined, each both before and after roasting.

TABLE IV.

Sugar found in coffee, before and after torrefaction.

	Sugar per Cent.	
	Raw.	Roasted.
1. Plantation Ceylon . .	7·52	1·14
2. „ „ . .	7·48	0·63
3. „ „ . .	7·70	0·0
4. „ „ . .	7·10	0·0
5. Native Ceylon . . .	5·70	0·46
6. Java	6·73	0·48
7. Costa Rica	6·72	0·49
8. „ „	6·87	0·40
9. Jamaica	7·78	0·0
10. Mocha	7·40	0·50
11. „	6·40	0·0
12. Neilgherry	6·20	0·0

The sugar in coffee appears to be increased by cultivation,—the proportion in Native Ceylon being 5·7 per cent., and in Plantation Ceylon from 7·1 to 7·7 per cent.

The proportion of sugar in the dried roots is high at first, and continues after roasting still very notable.

TABLE V.

Sugar in chicory and other sweet roots, before and after torrefaction.

	Sugar per Cent.	
	Raw.	Roasted.
Foreign chicory . . .	23·76	11·98
Guernsey chicory . . .	30·49	15·96
English chicory . . .	35·23	17·98
„ „ (Yorkshire) .	32·06	9·86
Mangold-wurzel . . .	23·68	9·96
Carrots (ordinary) . .	31·98	11·53
Turnips „ . . .	30·48	9·65
Beet root (red) . . .	24·06	17·24
Dandelion root . . .	21·96	9·08
Parsnips	21·70	6·98
Bouka (a coffee substitute) .	—	5·82

It thus appears that roasted chicory, as it is sold for mixing with coffee, retains from 9·86 to 17·98 per cent. of undecomposed sugar. In none of the other sweet roots which are occasionally substituted for chicory, such as mangold-wurzel, beet, turnip, or carrot, does the proportion of sugar retained after torrefaction fall under 9 per cent., with the exception of parsnip, in which the sugar falls to 6·98 per cent. The coffee substitute, "Bouka," falls into this class, and appears to be a mixture of true coffee with a torrefied sweet root.

The last group is composed of the leguminous and certain other seeds, with the cereals. The sugar was determined for most of these substances in the roasted form of the grain only, which alone affects the question of adulteration.

TABLE VI.

Sugar in various seeds, before and after torrefaction.

	Sugar per Cent.	
	Raw.	Roasted.
Acorns . . .	3·64	2·70
Horse-beans . .	—	1·62
Peas (grey) . .	—	1·08
Maize . . .	—	0·82
Rye-meal . . .	—	1·96
Bread-raspings . .	—	1·78
Lupin-seed . .	—	0·74
Brown malt . .	8·48	—
Black malt . . .	—	1·66

In the roasted seeds enumerated, the proportion of sugar is sensible, but not sufficiently considerable to give the means of distinguishing leguminous seeds and cereals from coffee. In roasted acorns, the sugar rises to 2·7 per cent., and black malt, it will be observed, still retains 1·66 per cent. of fermentable matter.

The fermentation test, on the other hand, is adapted to detect adulteration by chicory and the sweet roots, and will, we believe, from its certainty and facility of application, prove eminently useful for that purpose.

6. Coffee, and the various vegetable substances used in its adulteration, may be incinerated on a platinum or porcelain capsule, and leave an earthy ash, of which the composition is often characteristic of the plant. Valuable information may be obtained, without making a formal analysis of the ash, by simply digesting it in strong hydrochloric acid. The earth which remains undissolved after this treatment is silica. Now coffee, we find, is remarkably distinguished from the roots and cereals, by the small quantity of silica it affords. The quantity of that earth found in coffee is so small, that it may be doubted whether coffee contains any silica except what may accidentally adhere to the coffee beans, when collected, in the form of sand. The proportion of silica found in the twelve samples of coffee of Table IV. was as follows:—

TABLE VII.

Silica in roasted coffee.

	Per Cent. in Ash.
Sample 1	0·
„ 2	0·
„ 3	0·26
„ 4	0·02
„ 5	0·17
„ 6	0·28
„ 7	0·
„ 8	0·45
„ 9	0·
„ 10	0·
„ 11	0·
„ 12	0·09

The only case in which the silica approaches to half a per cent. of the ash is Sample 8; and in another sample of the same coffee, which was properly screened before roasting, the silica of the ash fell to 0.

On the other hand, the silica and sand, insoluble in acids, of four samples of roasted chicory, amounted to so much as 10·69,

13·13, 30·71, and 35·85 per cent. of the ash. It may be added, that the portion of this silica soluble in alkali was, in the same samples, 2·61, 3·81, 10·52, and 12·75 parts; the portion of silica insoluble in alkali, 8·08, 9·32, 20·19, and 23·10 parts.

The whole silica in roasted dandelion root amounted to 11·26 per cent. of the ash.

In other cultivated roots the proportion of silica does not appear to be so large as in chicory. The silica is always expressed with reference to 100 parts of the ash. Messrs. Way and Ogston find in the root of the carrot from 0·76 to 1·92 silica; in beet, from 1·4 to 4·11 silica; and in turnip, from 0·96 to 2·75 silica.

The proportion of silica appears to be low in certain grains and seeds, although rarely descending to the insignificant proportion of the coffee-bean,—and to be very high in other grains. We find in the ashes of acorns 1·01 per cent. of silica; in maize, 1·78 per cent. of silica; in the white lupin of the Levant, 0·87 per cent. of silica. Messrs. Ogston and Way report from 2·05 to 5·46 silica for wheat; from 23·6 to 70·77 silica for barley; from 38·48 to 50·03 for oats; and 9·22 for rye.

It appears, therefore, that the presence of 1 per cent. or upwards of silica in the ashes of coffee is a proof of adulteration; that the adulterating substances which increase the proportion of silica most considerably are oats and barley, then chicory and dandelion, which are followed by rye: wheat, beet, turnip, and carrot, would produce a small and less decisive effect.

There will now be presented complete analyses, made for this inquiry, of the ashes of seven varieties of coffee, and four different samples of chicory.

Table VIII.

Analyses of the ashes of coffee and chicory.

COFFEE.

	Plantation Ceylon	Native Ceylon	Java.	Costa Rica.	Jamaica.	Mocha.	Neilgherry.
Potash	55·10	52·72	54·00	53·20	53·72	51·52	55·80
Soda	—	—	—	—	—	—	—
Lime	4·10	4·58	4·11	4·61	6·16	5·87	5·68
Magnesia	8·42	8·46	8·20	8·66	8·37	8·87	8·49
Sesquioxide of iron	0·45	0·98	0·73	0·63	0·44	0·44	0·61
Sulphuric acid	3·62	4·48	3·49	3·82	3·10	5·26	3·09
Chlorine	1·11	0·45	0·26	1·00	0·72	0·59	0·60
Carbonic acid	17·47	16·93	18·13	16·34	16·54	16·98	14·92
Phosphoric acid	10·36	11·60	11·05	10·80	11·13	10·15	10·85
Silica	—	—	—	—	—	—	—
Sand	—	—	—	—	—	—	—
Total amount	100·63	100·20	99 97	99·06	100·18	99·68	100·04

CHICORY.

DEDUCTING SAND AND SILICA.

	Darkest English (Yorkshire)	English.	Foreign.	Guernsey.
Potash	38·53	27·85	46·07	46·27
Soda	9·34	16·90	3·17	5·49
Lime	10·79	10·81	7·78	7·65
Magnesia	6·06	8·08	5·33	5·55
Sesquioxide of iron	4·38	3·50	8·29	5·08
Sulphuric acid	11·38	11·78	8·38	8·67
Chlorine	5·67	5·23	5·03	6·58
Carbonic acid	2·04	3·22	4·36	4·60
Phosphoric acid	12·27	12·61	11·00	9·59
Silica	—	—	—	—
Sand	—	—	—	—
Total amount	100·46	99·98	99·41	99·48

DEDUCTING SAND AND NOT SILICA.

	Darkest English (Yorkshire)	English.	Foreign.	Guernsey.
Potash	37·07	27·13	40·20	41·41
Soda	8·99	16·46	2·77	4·92
Lime	10·38	10·53	6·79	6·85
Magnesia	5·83	7·87	4·66	4·97
Sesquioxide of iron	4·22	3·41	7·24	4·55
Sulphuric acid	10·95	11·48	7·32	7·76
Chlorine	5·46	5·10	4·39	5·89
Carbonic acid	1·97	3·14	3·81	4·12
Phosphoric acid	11·81	12·29	9·60	8·59
Silica	3·81	2·61	12·75	10·52
Sand	—	—	—	—
Total amount	100·49	100·02	99·53	99·58

NOT DEDUCTING SAND AND SILICA.

	Darkest English (Yorkshire)	English.	Foreign.	Guernsey.
Potash	33·48	24·88	29·56	32·07
Soda	8·12	15·10	2·04	3·81
Lime	9·38	9·60	5·00	5·31
Magnesia	5·27	7·22	3·42	3·85
Sesquioxide of iron	3·81	3·13	5·32	3·52
Sulphuric acid	10·29	10·53	5·38	6·01
Chlorine	4·93	4·68	3·23	4·56
Carbonic acid	1·78	2·88	2·60	3·19
Phosphoric acid	10·66	11·27	7·06	6·65
Silica	3·81	2·61	12·75	10·52
Sand	9·32	8·08	23·10	20·19
Total amount	100·85	99·98	100·66	99·68

The first difference which appears upon comparing the two sets of analyses is the absence of soda in coffee, and its presence in chicory to the extent of from 2·04 to 15·1 per cent. of the ash. The united amount of potash and soda does not differ much in the two substances. In chicory, the lime is greater and the magnesia less than in coffee. The sesquioxide of iron is strikingly different, being always under 1 per cent. in coffee, by our experiments, and ranging from 3·13 to 5·32 per cent. in chicory. The ash of chicory is, on this account, red to the eye when compared with that of coffee. The difference in chlorine is also important, the highest proportion observed in coffee-ash being 1·11 per cent., and the lowest proportion in chicory-ash 3·28 per cent. Coffee gives an ash which is highly carbonated, the carbonic acid varying from 14·92 to 18·13 per cent.; while the ash of chicory is only slightly carbonated, containing from 1·78 to 3·19 per cent. of carbonic acid. The proportion of phosphoric acid is pretty similar in the two kinds of ash. The disparity in the silica has been already referred to.

The differences most available in the two kinds of ash, as distinctive tests for coffee and chicory, appear to be the following:—

	In coffee-ash.	In chicory-ash.
Silica and sand .	—	10·69 to 35·85
Carbonic acid .	14·92 to 18·13	1·78 to 3·19
Sesquioxide of iron	0·44 to 0·98	3·13 to 5·32
Chlorine . .	0·26 to 1·11	3·28 to 4·93

Another series of ash analyses was executed, comprising the ash of the white lupin of the Levant—a seed which, from its chemical properties and low price, is not unlikely to be substituted for coffee—the ash of acorns, of maize, and of parsnip and dandelion roots.

TABLE IX.

Analyses of ashes of certain seeds and roots,

DEDUCTING SILICA, &c.

	Lupins.	Acorns.	Maize.	Parsnips.	Dandelion root.
Potash	33·83	55·49	31·28	56·86	20·22
Soda	17·90	0·63	—	—	34·87
Lime	7·81	6·98	3·11	6·88	12·87
Magnesia	6 23	4·36	14·98	6·52	1·47
Sesquioxide of iron . . .	—	0·54	0·85	0·53	1·42
Chlorine	2·12	2·53	0·50	2·10	4·32
Sulphuric acid	6·85	4·83	4·20	4·09	2·66
Carbonic acid	0·56	13·82	—	11·50	6·99
Phosphoric acid	25·74	11·26	45·29	13·91	12·63
Silica, &c.	—	—	—	—	—
Total amount	101·04	100·44	100·21	102·39	97·45

Analyses of ashes of certain seeds and roots,

NOT DEDUCTING SILICA, &c.

	Lupins.	Acorns.	Maize.	Parsnips.	Dandelion root.
Potash	33·54	54·93	30·74	56·54	17·95
Soda	17·75	0·63	—	—	30·95
Lime	7·75	6·01	3·06	6·85	11·43
Magnesia	6·18	4·32	14·72	6·49	1·31
Sesquioxide of iron	—	0·54	0·84	0·53	1·27
Chlorine	2·11	2·51	0·50	2·09	3·84
Sulphuric acid	6·80	4·79	4·13	4·07	2·37
Carbonic acid	0·56	13·69	—	11·44	6·21
Phosphoric acid	25·53	11·15	44·50	13·84	11·21
Silica, &c.	0·87	1·01	1·78	0·57	11·26
Total amount	101·09	99·58	100·27	102·42	97·80

In the ash only of the dandelion root is the silica sufficiently large in quantity to make a good distinction from coffee. Lupins and maize are distinguished from coffee by their low proportion of carbonic acid. The white lupin, both of the Levant and England, we find to contain a notable quantity of manganese. The oxide of iron is everywhere too low to be serviceable. Chlorine appears as low in maize as in coffee, but the proportion of that element is doubled in lupins, acorns, parsnips,—and nearly quadrupled in dandelion: a high proportion of phosphoric acid distinguishes maize, and we may add all the other cereals, from coffee.

The ash of the turnip root contains, according to Way and Ogston, from 9·54 to 14·82 per cent. of carbonic acid, which is very different from chicory, and nearly as high as in coffee. The sesquioxide of iron of turnip is also given even lower than in coffee, —from 0·14 to 0·66 per cent. Chlorine appears to be as abundant in the turnip, in the form of chloride of sodium, as in the chicory root.

According to the same excellent authorities, in beet-root-ash the carbonic acid varies from 15·23 to 21·61 per cent., and is therefore quite as high as in coffee-ash; the sesquioxide of iron, from 0·52 to 3·74 per cent., small as in coffee; the chlorine very large and distinctive, being represented by from 14·18 to 49·51 per cent. of chloride of sodium.

In the ash of the carrot, the carbonic acid is from 15·15 to 19·11 per cent.; the sesquioxide of iron, from 0·59 to 1·66 per cent.; chlorine nearly as in chicory, being represented by from 4·91 to 7·65 per cent. of chloride of sodium (Way and Ogston).

7. The action of the more ordinary chemical reagents upon infusions of coffee and chicory may now be noted. The indications thus obtained with coffee are unfortunately rendered much less characteristic by the torrefaction of the seed.

TABLE X.

Action of certain chemical reagents upon infusions of coffee and chicory.

	Raw Coffee.	Roasted Coffee.	Raw Chicory.	Roasted Chicory.
Potassa . .	A bright reddish-yellow liquid, and no precipitate.	Brownish-yellow liquid, and no precipitate.	Not altered.	Not altered.
Lime-water . .	Pale-yellow liquid; on standing, becoming green at the surface; no precipitate.	Reddish-brown, with shade of purple, and no precipitate.	Not altered.	Not altered.
Acetate of copper	Dirty-green precipitate.	Brownish-green precipitate.	Pale-green precipitate.	Gelatinous precipitate of a reddish-brown colour.
Perchloride of iron	Deep greenish-black precipitate.	Very dark greenish-black precipitate.	Blackish-brown-coloured liquid.	No effect.
Nitric acid . .	Bright red-coloured liquid.	Clear port-wine-coloured liquid.	No effect.	No effect at first; on standing, port-wine colour.
Sulphuric acid .	Dirty blackish-brown-coloured liquid.	Dark blackish-brown-coloured liquid.	Deep blackish-brown-coloured liquid.	Brownish-black liquid.
Hydrochloric acid	Pale brownish-yellow liquid.	Port-wine-coloured liquid.	No effect.	Slightly darkens the liquid.

In allowing a solution of unroasted coffee to stand, its green colour becomes gradually deeper. This change is due to oxidation and the formation of the viridic acid of Rochleder. It is greatly promoted by the presence of an alkali: an excess of lime brings out this colour very strongly in a day or two,—giving at first, however, a bright yellow colour. Subacetate of lead gives, in unroasted coffee, a yellow precipitate, which does not become green. An excess of acetate of copper gives a green precipitate

in abundance, which is brightened by the addition of an alkali. This copper precipitate has been used as a green pigment. The reactions above described are, however, much altered and obscured by the roasting of the coffee, and are therefore of little service for our present purpose.

It has already been stated that iodine produces no blue coloration in the infusion of either coffee or chicory. If the reagents named act clearly in a different manner upon any infusion from what they do upon pure coffee, a presumption of adulteration is obtained, but the indications must be of a positive and specific nature fully to establish adulteration.

8. Coffee was submitted to the usual process of distillation with soda-lime for the determination of its nitrogen. The proportion of nitrogen per cent. was, in coffee, Sample 1 (Table VII.), roasted, 2·93; in Sample 2, roasted, 2·62; in Sample 3, raw, 2·53, roasted, 2·70; in Sample 4, raw, 2·71; in Sample 5, raw, 2·50, roasted, 2·49. The proportion of nitrogen in roasted coffee appears therefore to lie between $2\frac{1}{2}$ and 3 per cent.

The nitrogen in a specimen of foreign chicory amounted, in the raw chicory, to 1·51 per cent.; in the same roasted, 1·42 per cent. The same of English growth gave, in the raw state, 1·86 per cent. of nitrogen; and in the roasted state, 1·74 per cent.

The proportion of nitrogen in coffee is therefore greater than in chicory; but the difference is not sufficiently marked to distinguish the two substances easily from each other. The conclusion may, however, be drawn, that less than 2 per cent. of nitrogen in coffee is a strong presumption of adulteration.

We may now advert to the peculiar and characteristic substances found in coffee, and the aid to be derived from them in the discovery of adulteration.

9. Professor **Rochleder**, who has devoted great attention to the analysis of coffee, gives the following enumeration of the substances found in the raw coffee-bean, with the formulæ of their elementary composition:—

		C.	H.	O.	N.
Woody fibre		12	10	10	
Cane sugar		12	11	11	
Fat	Palmitic acid	32	32	4	
	Oleic acid	36	34	4	
	Glycerine	6	8	6	
Legumin		48	36	14	6
Caffeic acid		16	7	6	
Caffeine		16	10	4	4

To these Rochleder had lately added citric acid ($C_{12}H_5O_{11}+3HO$), in the small proportion of 2 grains in a pound of coffee; also a trace, too small to be estimated by weight, of viridic acid ($C_{14}H_6O_7$). This last substance is the acid obtained by exposing solutions of the neutral and basic caffeates to the influence of the air. The green colour of raw coffee is believed by Rochleder to be owing to a small quantity of viridate of lime.

The evidence upon which Rochleder rests the existence of palmitic and citric acids in coffee does not appear to us quite decisive. The formulæ given by that chemist for both caffeic and viridic acids are doubtful.

It is also stated by Rochleder, that when dried caffeic acid is submitted to destructive distillation, a small quantity of crystals were obtained, which he considered to be pyrocatechine. The experiment repeated by us on a considerable scale gave a negative result.

Rochleder finds caffeic acid in Paraguay tea (*Ilex Paraguayensis*), as well as in coffee. This statement we must also doubt. The acid of the Paraguay tea has been examined by us, and found to have a certain resemblance to caffeic acid, but not to be identical with it. Free caffeic acid, when strongly heated in an open vessel, emits the peculiar odour of roasted coffee; but the acid from Paraguay tea emits a perfectly different odour when similarly treated.

The sugar of coffee may be inferred to exist in a peculiar condition, as was before hinted, from the fact that when the coffee is roasted, none of its sugar appears to be converted into grape-sugar, as it does not affect Trommer's test; while, when 7 grains of cane-sugar were added to 100 grains of coffee, and the whole roasted in the usual way, abundant indications of grape-sugar were obtained by the same test.

M. Payen gives the proportional quantities of the different substances which he finds in raw coffee as follows:—

Cellular tissue	34·000
Hygroscopic water	12·000
Fats	10· to 13·000
Starch, sugar, dextrin, and vegetable acids	15·500
Legumin	1·000
Chlorogenate of potash and caffeine	3·500
Nitrogenous portion	3·000
Free caffeine	0·800
Thick insoluble ethereal oil	0·001
Aromatic oil	0·002
Mineral constituents: potash, lime, magnesia, phosphorus, sulphur, silica, and traces of chlorine	6·697

Payen's chlorogenic acid is the same as the caffeic acid of Rochleder and Pfaff. Payen believed that he had obtained from coffee a crystalline double salt of this acid, containing potash and caffeine; but this observation has not been confirmed.

The proportion of fat in the coffee bean is remarkably high, being generally stated at 10 or above 10 per cent. We found at least 8·9 per cent. of fat readily extracted by ether. In chicory the proportion of natural fat is scarcely appreciable; but it is brought up by the fat added in the process of roasting the chicory.

10. Some uncertainty existing respecting the proportion of the active principle, caffeine, in coffee, the point was particularly inquired into. The following process was adopted:—The raw coffee was ground fine, having been previously well dried at 212° to facilitate that operation. A decoction was then made of 1000 grains, by the repeated application of boiling water, so as to exhaust the coffee of all soluble matter. The solution was concentrated a little by evaporation. The acid of the coffee, and certain other substances, were now entirely precipitated by the addition, first, of the neutral acetate of lead, and then of the subacetate of lead. These insoluble matters were removed from the liquid by filtration. The excess of lead in solution was then thrown down by means of hydrosulphuric acid.

The liquid, after this preparation, was evaporated to dryness, and the dry matter left was exhausted by means of strong spirit of wine (sp. gr. 0·840). The alcoholic solution was concentrated by evaporation, and allowed to stand in a nearly syrupy state for about ten days, in order to crystallise. The crystals, which are caffeine, were collected upon a small filter, and compressed powerfully to remove the mother liquor. These crystals were redissolved in a small quantity of water, the solution evaporated, and crystallised anew. It gave almost nothing but caffeine, in long silky white needles, with little or no colour. The proportion of caffeine obtained in five experiments, made upon different samples of coffee, was as follows:—

CAFFEINE IN RAW COFFEE.

In Native Ceylon . . .	0·80	per cent.
„ „ „ . . .	0·80	„ „
„ „ „ . . .	1·01	„ „
„ Plantation Ceylon . . .	0·54	„ „
„ „ „ . . .	0·83	„ „

The caffeine of the wild coffee appears to exceed that of the cultivated plant; the mean proportion of caffeine in Native Ceylon being 0·87 per cent., and in Plantation Ceylon 0·69 per cent.

The mean average of the whole five samples is 0·80 per cent. of caffeine. Probably the actual quantity of caffeine in the coffee bean is from 0·75 to 1 per cent., allowance being made for losses in the separation.

The proportion of theine (or caffeine) in tea is considerably greater, and more easily extracted. Two pounds of fine strong Congou yielded 2·93 grains of theine, or 2·09 per cent.

When it is merely desired to extract caffeine from raw or roasted coffee, without reference to quantity, the general process for the extraction of organic bases by means of ether suffices. Lime is added to the infusion of coffee, which is then evaporated to dryness upon a water-bath. The extract may be divided by means of clean sand, and then agitated with ether. The caffeine crystallises as the ether evaporates, or it may be re-dissolved in water, and crystallised again. We believe that the caffeine from 10 per cent. of coffee in a mixture might be extracted in sufficient quantity for its identification by the preceding simple process. Caffeine, when once obtained, is fully recognised by its easy sublimation, and also by its action with nitric acid, in which it resembles uric acid. When the solution of caffeine in nitric acid is evaporated to dryness, and exposed to ammoniacal gas, it is covered by a pink blush, like murexide.

The only other substances besides coffee in which caffeine is known to exist, are tea, Paraguay tea, and a species of chocolate made from the *Gaurana officinalis* or *Paullinia sorbilis*.

11. Chemists generally are disposed to refer the flavour and peculiar properties of coffee, as a beverage, more to its acid—the *caffeic acid* (particularly after that substance is modified in its properties by roasting), than to any other constituent of the seed. Rochleder considers this acid as belonging to the tannin class of substances, and calls it tanno-caffeic acid. But as caffeic acid does not precipitate gelatine, it is deficient in the most characteristic quality of the tannic acids. Caffeic acid, in the present state of our knowledge, appears to be confined to the coffee plant.

We have observed a property of caffeic acid which facilitates the detection of that substance, and consequently of coffee, in a mixture. Caffeic acid appears to be analogous to kinic acid, the acid of cinchona barks, for it yields kinone when oxidated by means of sulphuric acid and binoxide of manganese. To observe this property, the coffee is boiled with water and a little slaked lime, the infusion filtered, and evaporated down to the consistence of a syrup. The syrupy liquid is then mixed in a retort with four times its weight of binoxide of manganese, and 1 part of oil of vitriol diluted with an equal bulk of water. Sufficient heat is

produced by the action of sulphuric acid upon the other materials, to bring over the greater portion of the kinone, and the lamp need not be applied till towards the close of the operation. The distillate consists of yellow crystals of kinone, which usually coat the neck and sides of the retort, and a bright yellow liquid, which is a saturated aqueous solution of kinone, with a considerable quantity of formic acid. Kinone is easily discernible by its volatility and peculiarly acrid odour, which greatly resembles that of chlorine. The solution of kinone gives with ammonia a sepia-black colour, and becomes reddish-brown with hydrosulphuric acid. It is decolorised by sulphurous acid. The beautiful green hydrokinone is obtained by exactly neutralising the solution of the yellow kinone with sulphurous acid, great care being taken not to introduce the latter in excess.

The peculiar acid of Paraguay tea agrees with caffeic acid (to which it is no doubt related) in yielding kinone to similar oxidising agencies: so does the acid of the leaves of common holly (*Ilex aquifolium*), tea, and the whole of the *cinchona* tribe.

The *prune* tribe of plants, including the sloe, cherry, laurel, &c., the seeds of which yield prussic acid, all contain amygdalin, or some similar principle. Now all of these, when oxidised in the same manner as the former class, yield oil of bitter almonds, and so can be recognised.

The *willow* and *poplar* tribe, on the other hand, yield oil of *Spirea ulmaria* (salicylous acid), a very characteristic substance.

The tests for kinone can be applied in a few minutes, and they are sufficient to indicate the presence of 10 or 12 per cent. of coffee in a mixture.

12. The root of *chicory* presents no feature of a marked nature, beyond its large proportion of sugar and the composition of its ash, which have both been sufficiently adverted to. The proportion of fat naturally in the root is quite insignificant. In an infusion of the fresh undried root, neutral acetate of lead appears to throw down the whole acids of chicory, and the subacetate of lead produces no further precipitate in the liquid. But the root appears to undergo a considerable modification by being dried at a temperature not exceeding 212°. Its infusion now gives a second precipitate with subacetate of lead following the neutral acetate. Both of these precipitates can be well enough washed; but when the attempt was made to decompose either of them by means of hydrosulphuric acid, a mucilaginous liquid was obtained, from which the sulphide of lead does not fall, unless with a considerable addition of alcohol. The acid precipitates appear most indeterminate, and afford nothing crystalline. A great deal of pectin-looking substance is present. Chicory also appears to

possess about one-fourth of the quantity of inulin that is contained in the dahlia root, and starch in no other form, the infusion of chicory giving only a brown with iodine, and no blue. Chicory appears to contain no oxalic, malic, citric, or any other crystallisable organic acid. The other sweet roots, beet, turnip, &c., also, like chicory, present little that is tangible in their chemical properties. But the high colour of the infusions of all these roots when roasted, the great density of their solutions, and their fermentability, afford sufficient means for distinguishing them from coffee, and for discovering their admixture with that substance.

The properties of a great variety of other vegetable substances, which might possibly be employed in the adulteration of coffee, are exhibited in the early tables of this Report.

On Circumstances modifying the Action of Chemical Affinity.*

By J. H. Gladstone, Ph.D., F.R.S.

It is among the facts in chemical science which admit of no dispute, that a substance frequently shows a greater tendency to combine with one body than with another. This has usually received the appellation "elective attraction," or "elective affinity." It is also perhaps universally allowed that the manifestations of this elective affinity are greatly influenced by the insolubility or the volatility of the original substances, or of the resulting compounds. The degree of temperature, the respective masses of the different substances, the presence of other bodies, and many circumstances beside these, are supposed to modify the result.

The attempt has frequently been made to construct tables showing the relative strength of affinity of different substances for some particular body, and Guyton de Morveau even endeavoured to give a numerical expression to them. In treating of this subject, the elaborate disquisition of Bergman, "De Attractionibus Electivis," must be referred to; in which he illustrates at once the chemical fact, and the meaning of the term, by supposing A to be a substance united to *c*, and that, on the addition of *b*, the *c* is excluded, and the union of the latter substance with A is brought about; in which case, he says, *b* has a stronger elective attraction for A than *c* has. He, in common with most chemists, both of his own and of later times, takes it for granted that if *b* decomposes A*c*, it does so completely. The Swedish chemist

* Phil. Trans. 1855, p. 179.

gives the results of nearly 2000 reactions in one table, the first column of which exhibits the following substances arranged according to their affinity for sulphuric acid, commencing with what he conceived the most powerful:—baryta, potash, soda, lime, magnesia, ammonia, zinc, manganese, iron, lead, tin, cobalt, copper, nickel, bismuth, arsenic, mercury, antimony, silver, gold, platinum, alumina, sesquioxide of iron, water, phlogiston. The suitability of some of the methods employed for arriving at these results, has never, as far as I know, been questioned; for instance, that zinc has a stronger affinity for sulphuric acid than manganese, or iron, or lead has, because it will separate any one of these metals from its solution in the said acid. Other methods, however, are more open to objection,—such, for example, as that which led Bergman to place baryta at the head of the series, because it took sulphuric acid from every other base. To such deductions as this, drawn from precipitation, it may be objected that the tendency of the two bodies to combine has arisen more or less from the insolubility of the compound. Berthollet adopted this view, and in his "Recherches sur les Lois de l'Affinité" he endeavoured to prove "que les affinités électives n'agissent pas comme des forces absolues par lesquelles une substance seroit déplacée par une autre dans une combinaison; mais que, dans toutes les compositions et les décompositions qui sont dues à l'affinité élective, il se fait un partage de l'objet de la combinaison entre les substances dont l'action est opposée, et que les proportions de ce partage sont déterminées, non seulement par l'énergie de l'affinité de ces substances, mais aussi par la quantité avec laquelle elles agissent, de sorte que la quantité peut suppléer à la force de l'affinité pour produire un même degré de saturation."

These two conflicting views were much discussed at the time when they were propounded; the attention subsequently paid to the laws of stoïchiometry has removed much of the difficulty in which the subject was then involved; Gay-Lussac has pointed out the erroneous idea of cohesion that obscured the reasoning of Berthollet; and yet the amount of truth contained in either of these opposite opinions remains still an open question.

It is now some years since I first began to reason, and occasionally to experiment, upon this subject. Since that time, Malaguti has published a paper bearing upon it, which will be referred to subsequently; Bunsen and Debus have experimented, and independently arrived at a very remarkable law; and Williamson has on more than one occasion vindicated the views of Berthollet.

Bunsen* exploded together carbonic oxide, hydrogen, or

* Ann. Ch. Pharm. lxxxv. 137.

cyanogen with oxygen, and, after varying his experiments greatly, deduced conclusions tending to show a simple atomic relation between the products of the combustion, and a sudden transition from one ratio to another, as the proportions of the original gases were varied. Debus * examined the phenomena presented in the precipitation of a mixture of the hydrates of lime and baryta by carbonic acid, and of the hydrochlorates of these earths by carbonate of soda, and arrived at analogous results.

In each of these cases, however, the first products of the chemical combination were removed at once from the field of action. It is evidently quite another case when the products themselves remain free to react. A mixture of two salts in solution, which do not produce a precipitate, affords a case where this requisite is fulfilled. Let AB and CD be such salts. According to the one view, when mixed, they will either remain without mutual action, or, should the affinities so preponderate, they will become simply AD and CB, the excess of either original salt remaining inactive. According to the other view, A will divide itself in certain proportions between B and D, while C will do the same in the inverse ratio, the said proportions being determined not solely by the differences of energy in the affinities, but also by the differences of the quantities of the bodies. Again, supposing the latter view to be correct, another question will arise, — Does the amount of AD or CB produced increase in a gradual manner with the relative increase of AB; or do sudden transitions take place under these circumstances, such as Bunsen and Debus observed in their experiments?

It was to the elucidation of these questions that I applied myself. In the majority of instances, it is impossible to ascertain what has taken place when a mixture of the kind alluded to has been made; but the physical properties of salts will sometimes give an indication. Colour seemed to offer the best means of solving the problem; yet even here a difficulty arose from the fact that many bases, such as nickel, give the same-coloured solution when combined with different acids, and *vice versâ*. Sesquioxide of iron, however, appeared to promise good results, since many of its salts are intensely coloured, while others are almost colourless.

FERRIC SULPHOCYANIDE.

If a soluble sulphocyanide be mixed with a ferric salt, a red solution results, indicating the formation of the ferric sulphocyanide. Suppose three equivalents of the sulphocyanide be

* Ann. Ch. Pharm. lxxxv. 103; lxxxvi. 156; lxxxvii. 238.

mixed with one equivalent of the metallic salt, we have the exact proportions theoretically necessary for the production of Fe_2, $3S_2$ Cy. The first question to be solved is,—In such a case does the whole of the iron and of the sulphocyanogen combine as ferric sulphocyanide, or does it not? If Bergman's view be correct, the decomposition will be in accordance with the following simple formula (Rd standing for any salt radical, and M for any metal)—

$$Fe_2\,Rd_3 + 3MS_2Cy = Fe_2,\ 3S_2Cy + 3MRd;$$

and it will not matter what metal is represented by M, or what salt radical by Rd, provided only that a double decomposition *does* take place. Besides which, the addition of a larger quantity of either one of the original compounds will not increase the colour; for there is but one sesquisulphocyanide of iron, and the whole of the iron, or of the sulphocyanogen (as the case may be), has been already saturated. If, however, Berthollet's view be correct, the decomposition will not be so complete as to form merely Fe_2, $3S_2$ Cy and 3M Rd, but in addition to these two salts there will be certain portions of the two original salts still remaining as such in the solution. This will become manifest by an amount of colour being obtained which is not equal to what would have been produced had the whole of the iron entered into combination with the sulphocyanogen: and the requirements of the theory will lead us moreover to expect that the amount of ferric sulphocyanide (and consequently the depth of colour) will depend in a great measure on the nature of M or Rd, and will be increased by each addition of either the soluble sulphocyanide or the ferric salt.

The following were the preliminaries for the complete determination of this question:—

Aqueous solutions of the ferric chloride, nitrate, sulphate, acetate, and citrate, were prepared of known strength; as, also, of sulphocyanide of potassium, barium, and mercury; of hydrosulphocyanic acid, and of various potash salts.

In order to compare the depth of colour produced on the admixture of these solutions, it was necessary to have vessels of colourless glass of a uniform character. Ordinary precipitating glasses, holding about five ounces, were found peculiarly fitted for the purpose: being blown, and not moulded, they are very translucent; they are easily obtained devoid of colour; and, although not strictly uniform in size, it was easy to pick out a sufficient number which would furnish every requisite for the experiment. This was tested by dividing a coloured solution into two equal parts, and pouring one-half into one glass, and the other half into another: if the two solutions appeared then of a perfect equality of tint, nothing more could be desired. When two or more coloured solutions were to be compared, the best method was

found to be to place the glasses containing them on a stand before the window, across the pane of which was stretched a piece of tissue-paper about three inches in depth. The experiments were almost always performed when the sun was shining, but not on the window itself, as that was found to be disadvantageous. By observing the coloured solutions against the evenly illuminated tissue-paper, most exact results could be obtained, especially after a little practice. If the object was to observe the amount of dilution necessary to reduce one coloured solution to the same tint as another, distilled water was added, and thoroughly mixed with it, until equal bulks of the two solutions appeared alike. The amount of water added was of course easily measured in a graduated vessel. My own observation was always checked by that of my assistant; and if we differed, I generally adopted his view, since, having no idea of what result was to be expected, his judgment was the more impartial. I may also state in this place, that it was found unnecessary to let a freshly mixed solution containing a sulphocyanide stand any length of time, for it assumed instantaneously its proper amount of colour: two mixtures, similarly prepared, were always found to be of precisely the same shade; and everything conspired to give me great and increasing confidence in the validity of testimony drawn from the colour of a solution.

The first object to be determined evidently was, whether, on mixing three equivalents of sulphocyanide of potassium with one equivalent of the ferric salt, say the chloride, the full depth of colour possible from the combination of all the sulphocyanogen with all the iron was actually obtained. That this was not the case was seen at once, for on adding to such a mixture either more sulphocyanide of potassium, or more chloride of iron, the colour was increased. This showed also the influence of mass, which will be exhibited quantitatively in due course; but before doing so it is necessary to advert to another part of the inquiry, viz.—

The dependence of the amount of the coloured salt on the nature of the other substances present in the solution, but which are not immediately concerned in its formation.—In order to investigate this point, solutions of each of the ferric salts, containing exactly the same amount of iron, were mixed with the sulphocyanide of potassium solution, in the proportion of one equiv. of the former to three of the latter. The five mixtures were equally diluted. At a glance it was evident that a widely different amount of red sulphocyanide of iron had been formed. The solution containing the ferric citrate was still green; that containing the acetate was red, but by no means deep in colour, and of a yellowish tint; while those containing the sulphate, nitrate, or chloride, were of an intense red. The following are the relative amounts of dilu-

tion required to bring these four last-mentioned solutions to the same tint: —

3 equivalents sulphocyan. potassium + 1 equivalent ferric nitrate diluted to 100 parts.
3 equivalents sulphocyan. potassium + 1 equivalent ferric chloride diluted to 89·4 parts.
3 equivalents sulphocyan. potassium + 1 equivalent ferric sulphate diluted to 65·2 parts.
3 equivalents sulphocyan. potassium + 1 equivalent ferric acetate diluted to 20 parts.

The numbers 100, 89·4, 65·2, and 20 therefore represent the relative amounts of the ferric sulphocyanide contained in these several mixtures.*

In reference to the mixture of ferric citrate with sulphocyanide of potassium, the question presents itself, — Does absolutely no interchange take place between them, or does a partial though very minute formation of ferric sulphocyanide occur, in accordance both with the law of Berthollet and the analogy of the other cases? The latter conclusion will appear probable from the following observations. Although the yellowish-green tint of the citrate still remains after the addition of three equivalents of the sulphocyanide, six equivalents almost remove it, and a larger quantity renders the solution colourless. No red colour ever appears in a very dilute solution, but this destruction of the green appears to point to the presence of a sufficient amount of the complementary colour to neutralise it; and if sulphocyanide of potas-

* After this paper had been read, the following note was appended: — That two or more solutions of the same salt in the same solvent, and of equal depth of colour, are of the same strength, requires no proof. Hence I apprehend no objection can be raised against the conclusion that the gross amounts of salt dissolved in the different solutions are directly proportional to their volume. But it may be objected, that though this is true of the solutions when diluted to an equality of colour, it is not necessarily true of the solutions before they were diluted, for the solvent may exercise some chemical action on the coloured salt, absolutely increasing or diminishing its quantity. Should such be the case, it appears to me actually the most correct plan of proceeding to reckon the result when the solutions of the coloured salt are of equal strength,—that is to say, when the solvent is in each case in the same proportion to the dissolved salt; for the disturbing influence of the solvent is thus practically got rid of, by its reduction to an equality in all the solutions compared.

There is, however, a more serious objection,—namely, that the solvent may act differently on the coloured salt, according to the nature or the quantity of the colourless salts present at the same time in the several solutions; or that these salts may act differently according to the amount of solvent with which they are conjoined. That this may be the case to a slight extent is very possible, but the experiment recorded on page 79 shows that it was too inconsiderable to be appreciated in the cases there submitted to examination. As this is an important matter, I have repeated the experiment in a great variety of ways, and have satisfied my mind that the amount of error arising from this cause must be quite insignificant — at any rate as far as the ferric sulphocyanide is concerned. The slight differences that do occur are rather in the character than in the intensity of the colour.

sium be added in large excess to a strong solution of citrate of iron, an unmistakeable red ensues.

Similar experiments were tried in which the same ferric salt was employed, but different sulphocyanides. Two portions of nitrate of iron, each representing one equivalent, were mixed, the one with six equivalents of sulphocyanide of barium, the other with a corresponding amount of the potassium salt. A deep red resulted in both instances, but 1000 gr. meas. of the solution containing the potassium compound required the dilution of that containing the barium salt to only 880 gr. meas. to bring it to an equality of colour. The solution of sulphocyanide of mercury produced a scarcely perceptible reddening when added to the ferric nitrate.

These experiments suffice to show, that on mixing together solutions of soluble sulphocyanides and of ferric salts, the amount of sesquisulphocyanide of iron formed depends in a great measure on the nature of the substances previously combined with the sulphocyanogen and with the metallic oxide. The question naturally arises,—Does the converse of this hold good? If a solution of sesquisulphocyanide of iron be mixed with some other salt, not capable of forming a precipitate with it, will that also cause the distribution of the elements into *four* salts, manifesting itself by a diminution of the colour? and if so, will that vary according to the nature of the other salt?

	I.	II.	III.	IV.
Volume of original solution + salt added .	70 m.	64 m.	34 m.	60 m.
Mixture containing the nitrate . . .	80	77	41	62
Mixture containing the chloride . .	90	90	56	68
Mixture containing the sulphate . .	150	160	124	85
Mixture containing the acetate . .	270	220	164	120
Mixture containing the citrate . . .	trace of red	green		

Six equal portions of as pure sesquisulphocyanide of iron as could be prepared were taken: one was kept as a standard; to the other five were added respectively equal portions of the nitrate, hydrochlorate, sulphate, acetate, and citrate of potash. In each case, the colour was reduced. Column I. in the annexed table shows the amount to which the standard had to be diluted before it was brought down to an equality in colour with the different mixtures. Column II. represents a similar experiment, in which a red mixture of one equivalent of sesquichloride of iron and twelve equivalents of sulphocyanide of potassium was employed

instead of the actual ferric sulphocyanide. In III. a mixture of ferric sulphate and sulphocyanide of potassium was employed; in IV. the same, with a large excess of sulphuric acid.

These experiments might be varied *ad infinitum*, all proving the influence on the resulting colour of the *nature* of a substance mixed with the ferric sulphocyanide. Other organic acids, such as the oxalic and the tartaric, were found to reduce the red very rapidly.* As might be expected, also, the diversity of effect is not confined to differences in the *acid* present. The addition of a protosalt of iron has a very great effect in reducing the colour of the ferric sulphocyanide: baryta and lime salts act powerfully. A solution of chloride of mercury (as was observed long ago) very speedily removes the colour.

The colour of a mixture not dependent on the manner in which the constituents were originally arranged.—On more closely examining the above results, it will be seen that whether ferric citrate be mixed with sulphocyanide of potassium, or ferric sulphocyanide with citrate of potash, the resulting liquids contain but the merest trace of the red salt; it appears also that the deepest colour is obtained on mixing either ferric nitrate with sulphocyanide of potassium, or ferric sulphocyanide with nitrate of potash; whilst the mixtures containing compounds of acetic, sulphuric, and hydrochloric acids are intermediate in colour in regular order. Mercury also seems to exert the most powerful affinity for sulphocyanogen in whatever way they are brought together. This suggests the conclusion that the amount of sulphocyanide of iron in a mixture of salts does not depend on the *manner* in which the different substances were at first combined. The experiment above described was incapable of affording a quantitative demonstration of this, as a perfectly pure and definite sulphocyanide of iron was not obtained; but the following arrangement was made to put it to a rigid test. Two mixtures were made of the solutions of known strength, so that each contained one equivalent of ferric oxide, three equivalents of potash, three equivalents of nitric acid, and three equivalents of sulphuric acid. To each was added 1·5 equiv. of sulphocyanide of potassium. The colours resulting in the two cases were so nearly identical, that the first diluted to 1770 gr. meas. just equalled the second diluted to 1820 gr. meas. Another 1·5 equiv. of sulphocyanide of potassium was added to each. The two solutions appeared now identical in colour; they certainly did not differ by 1 degree in 80. The amount of sulphocyanide of potassium in each was then doubled: the resulting colours could not be distinguished from each other. It appears, there-

* Pelouze has observed the different effects of different acids, Ann. Chim. et Phys. xliv. 216.

fore, that it makes no difference whether there be mixed in solution

$Fe_2O_3, 3NO_5 + 3(KO, SO_3) + 3KS_2$ Cy or $Fe_2O_3, 3SO_3 + 3(KO, NO_5) + 3KS_2$ Cy.

The influence of the mass of one of the substances that produce the coloured salt.—The influence of mass has yet to be considered quantitatively. For this purpose, two mixtures were prepared, each containing one equiv. of the ferric nitrate, and three equivs. of the sulphocyanide of potassium solution. They were both diluted so as to occupy the same volume. The one was kept as a standard of comparison; with the other, additional portions of sulphocyanide of potassium were mixed; and as that increased the colour, it was diluted till brought to an equality with the standard solution.

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv. +	3 equivs.	88	1 equiv. +	63 equivs.	356
1 equiv. +	6 equivs.	127	1 equiv. +	99 equivs.	419
1 equiv. +	9·6 equivs.	156	1 equiv. +	135 equivs.	457
1 equiv. +	12·6 equivs.	176	1 equiv. +	189 equivs.	508
1 equiv. +	16·2 equivs.	195	1 equiv. +	243 equivs.	539
1 equiv. +	19·2 equivs.	213	1 equiv. +	297 equivs.	560
1 equiv. +	28·2 equivs.	266	1 equiv. +	375 equivs.	587
1 equiv. +	46·2 equivs.	318			

On comparing these numbers, it will be at once evident that each addition of the sulphocyanide produced relatively a smaller increase of colour. In the full paper, these results, and those of a similar character which follow, are represented by curves, of which the ordinates express the proportionate amount of red salt, and the abscissæ the number of equivalents of the sulphocyanide added.

The influence of mass was again tried by means of additional portions of ferric nitrate instead of additional sulphocyanide of potassium. The following are the results of the observations reduced as before:—

Sulphocyan. of potassium.	Ferric nitrate.	Red salt produced.	Sulphocyan. of potassium.	Ferric nitrate.	Red salt produced.
3 equivs. +	1 equiv.	88	3 equivs. +	5 equivs.	138
3 equivs. +	2 equivs.	110·5	3 equivs. +	6 equivs.	144
3 equivs. +	3 equivs.	122	3 equivs. +	10 equivs.	161
3 equivs. +	4 equivs.	131	3 equivs. +	14 equivs.	174

It is not difficult to bring this experiment into uniformity with the preceding so as to form in fact a continuation of it, one equiv. of ferric nitrate being combined with less than three equivs. of sulphocyanide of potassium. For, expressing the number of equivalents of the iron salt by x, and the comparative amount of ferric sulphocyanide by y, the general formula of the terms in the above table will be, K denoting the potassium and F the iron salt,—

$$3K+xF=y,$$

which may evidently be reduced to a unity of F by dividing by x, thus—

$$F+\frac{3}{x}K=\frac{y}{x}.$$

On this principle the experiment may be thus tabulated:—

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.	+ 3 equivs.	88	1 equiv.	+ 0·6 equiv.	27·6
1 equiv.	+ 1·5 equiv.	55·25	1 equiv.	+ 0·5 equiv.	24
1 equiv.	+ 1 equiv.	40·66	1 equiv.	+ 0·3 equiv.	16·1
1 equiv.	+ 0·75 equiv.	32·75	1 equiv.	+ 0·21 equiv.	12·43

It need scarcely be explained, that had the whole of the sulphocyanogen present in the above experiment united itself with the iron, the second term would have indicated 44 degrees instead of 55·25, the third 29·33, and so on.

In order to confirm, by a more direct experiment, the result just arrived at, two mixtures were made, consisting of 1 equiv. of ferric nitrate, and 0·24 equiv. of sulphocyanide of potassium. The experiment was conducted as in the previous cases.

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.	+ 0·24 equiv.	19	1 equiv.	+ 3·57 equivs.	97·8
1 equiv.	+ 0·48 equiv.	29·7	1 equiv.	+ 4·44 equivs.	108·2
1 equiv.	+ 0·78 equiv.	39·4	1 equiv.	+ 5·58 equivs.	119
1 equiv.	+ 1·05 equiv.	48·7	1 equiv.	+ 7·08 equivs.	134·3
1 equiv.	+ 1·31 equiv.	60·2	1 equiv.	+ 8·64 equivs.	147·3
1 equiv.	+ 1·83 equiv.	69	1 equiv.	+ 10·29 equivs.	158·1
1 equiv.	+ 2·22 equivs.	76·5	1 equiv.	+ 11·79 equivs.	167·8
1 equiv.	+ 2·88 equivs.	86·3			

The regularity of this increase of colour (as exhibited to the eye in the curves) is a proof that no law obtains under the circumstances of the experiment, similar to that observed and enunciated by Bunsen. There is nowhere any sudden increase in the amount of ferric sulphocyanide formed. If the partition of the bases and acids in the mixture really take place at first in atomic proportions, it is evident that, being at full liberty to act and react, the salts arrange themselves according to their respective mass, without reference to their respective atomic weights.

The effect of mass on the formation of ferric sulphocyanide in a mixture of salts, where other substances replaced the nitric acid or the potash, was also tried.

The two following tables represent similar experiments with the ferric sulphate and chloride.

Ferric sulphate.	Sulphocyan. of potassium.	Red salt produced.	Ferric sulphate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv. +	3 equivs.	88	1 equiv. +	45 equivs.	318
1 equiv. +	6 equivs.	128	1 equiv. +	57 equivs.	355
1 equiv. +	9 equivs.	153	1 equiv. +	69 equivs.	390
1 equiv. +	12 equivs.	177	1 equiv. +	81 equivs.	418
1 equiv. +	15 equivs.	198	1 equiv. +	93 equivs.	440
1 equiv. +	20 equivs.	223	1 equiv. +	105 equivs.	458
1 equiv. +	24 equivs.	241	1 equiv. +	123 equivs.	486
1 equiv. +	30 equivs.	263	1 equiv. +	147 equivs.	513
1 equiv. +	36 equivs.	288	1 equiv. +	195 equivs.	538

Ferric chloride.	Sulphocyan. of potassium.	Red salt produced	Ferric chloride.	Sulphocyan. of potassium.	Red salt produced.
1 equiv. +	3 equivs.	88	1 equiv. +	65·4 equivs.	338
1 equiv. +	9 equivs.	148	1 equiv. +	83·4 equivs.	370
1 equiv. +	15 equivs.	190	1 equiv. +	107·4 equivs.	400
1 equiv. +	21 equivs.	216	1 equiv. +	131·4 equivs.	428
1 equiv. +	28·8 equivs.	246	1 equiv. +	155·4 equivs.	456
1 equiv. +	41·4 equivs.	286	1 equiv. +	191·4 equivs.	488
1 equiv. +	53·4 equivs.	312	1 equiv. +	239·4 equivs.	528

A glance at these tables will show that, although the actual amount of ferric sulphocyanide produced from the same quantity of the sesquinitrate, chloride, or sulphate of iron, varies greatly,

yet the increase of colour on the addition of more sulphocyanide of potassium maintains a somewhat similar ratio in each case. The variations that do exist, arise, I am disposed to think, mainly from errors in the experiment; and this opinion is founded not only on the observations above detailed, but upon others of a shorter range, which it was not considered necessary to record, especially as the three given were the last of their respective kinds which I made, and on that account, I believe, worthy of the greater reliance. None of the others, I may remark, differed materially from them.

I have in vain endeavoured, by the aid of my friend, Mr. Henry Watts, to find an equation which will resolve the curves deduced from the above observations. They do not appear to belong to the second order.

For the purpose of seeing whether the same ratio was maintained where a much smaller proportion of red sulphocyanide was formed, the experiment was repeated with the ferric acetate.

Ferric acetate.	Sulphocyan. of potassium.	Red salt produced.	Ferric acetate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.	+ 1 equiv.	62·4	1 equiv.	+ 11 equivs.	232
1 equiv.	+ 3 equivs.	88	1 equiv.	+ 13 equivs.	304
1 equiv.	+ 5 equivs.	108	1 equiv.	+ 15 equivs.	352
1 equiv.	+ 7 equivs.	133	1 equiv.	+ 19 equivs.	398
1 equiv.	+ 9 equivs.	187			

Here we have not only an entirely different ratio, but one of an irregular character. It is evident there is some interfering action; what that is will be seen when the ferric acetate itself is made the subject of experiment.

A similar experiment on the influence of mass was tried with hydrogen in the place of potassium.

Ferric nitrate.	Hydrosulphocyanic acid.	Red salt produced.	Ferric nitrate.	Hydrosulphocyanic acid.	Red salt produced.
1 equiv.	+ 2 equivs.	66	1 equiv.	+ 20 equivs.	288
1 equiv.	+ 4 equivs.	108	1 equiv.	+ 24 equivs.	315
1 equiv.	+ 6 equivs.	142	1 equiv.	+ 30 equivs.	353
1 equiv.	+ 8 equivs.	168	1 equiv.	+ 38 equivs.	400
1 equiv.	+ 12 equivs.	217	1 equiv.	+ 46 equivs.	440
1 equiv.	+ 16 equivs.	257			

The ratio here is regular, but more rapid than in the case of the potassium salt.

Method of determining the actual amount of the coloured salt in a given mixture.—From the experiments above recorded, it would seem probable that no amount of sulphocyanide of potassium added to a ferric salt will absolutely convert the whole of it into the sesquisulphocyanide of iron. Yet we can easily judge where this result will be very nearly attained. Thus 400 equivalents of the sulphocyanide, added to one of the ferric nitrate, must give a close approximation. A somewhat larger quantity will do the same with the sulphate. Indeed, it was found by experiment that 500 equivalents of the sulphocyanide added to each of the three principal ferric compounds, caused as nearly as possible the same intensity of colour. Such a mixture was made, assumed to be the proper tint for an equivalent of the ferric sulphocyanide, and employed as a standard. Mixtures were then made of three equivalents of sulphocyanide of potassium with one equivalent of the various ferric salts, each occupying 330 gr. meas. The standard red was then diluted till it was equal in colour to these several mixtures. The annexed table gives the different amounts of dilution required.

1 eq. ferric nitrate + 3 eq. sulphocy. of potas. 1700 gr. m.
1 eq. ferric chloride + 3 eq. sulphocy. of potas. 1900 gr. m.
1 eq. ferric sulphate + 3 eq. sulphocy. of potas. 2650 gr. m.
1 eq. ferric acetate + 3 eq. sulphocy. of potas. 7000 gr. m. (about).

This affords us the elements requisite for a calculation of the actual amount of ferric sulphocyanide present in each of these mixtures; and had it been desirable, almost every observation given above might have been thus reckoned. The ratio between the volumes of the diluted standard ferric sulphocyanide, and that of any one of the other red mixtures (330 gr. meas.), gives the ratio between one equivalent and the fractional part existing in the said mixture. The four observations calculated on this principle give the following results: —

1 equiv. ferric nitrate + 3 equivs. sulphocyanide of potassium give 0·1941 equivalent ferric sulphocyanide.
1 equiv. ferric chloride + 3 equivs. sulphocyanide of potassium give 0·1737 equivalent ferric sulphocyanide.
1 equiv. ferric sulphate + 3 equivs. sulphocyanide of potassium give 0·1245 equivalent ferric sulphocyanide.
1 equiv. ferric acetate + 3 equivs. sulphocyanide of potassium give 0·0471 equivalent ferric sulphocyanide (about).

If this mode of reckoning involve no fallacy, the proportion between these four numbers should be the same as that given near

the commencement of this inquiry, where the colours produced on a different occasion by adding three equivalents of sulphocyanide of potassium to one equivalent of the ferric salts, were directly compared. That they do agree almost exactly will be seen from the following table, where column I. gives the numbers of the former experiment, and column II. those of the last calculation reduced to the same unit of comparison.

	I.	II.
1 equiv. ferric nitrate + 3 equivs. sulphocyanide of potassium	100	100
1 equiv. ferric chloride + 3 equivs. sulphocyanide of potassium	89·4	89·5
1 equiv. ferric sulphate + 3 equivs. sulphocyanide of potassium	65·2	64·2
1 equiv. ferric acetate + 3 equivs. sulphocyanide of potassium	20	24·2?

This close agreement proves not only the correctness of the two independent experiments, but also the correctness of this method of reckoning the amount of the coloured salt in any given mixture.

Influence of the mass of a substance present in the solution, but which is not one of the constituents of the coloured salt.—It has already been remarked that the addition of a colourless salt will reduce the colour of a solution of ferric sulphocyanide. The influence of mass in this kind of action remains to be examined.

A mixture was made of ferric sulphate and sulphocyanide of potassium. The red solution that resulted contained of course sulphate of potash. Successive portions of a solution of this salt were added, and the amount of decomposition effected was determined by means similar to those employed in previous experiments.

Sulphate of potash added.	Water added to comparative solution.	Sulphate of potash added.	Water added to comparative solution.
5 measures	= 22 measures.	30 measures	= 92 measures.
10 measures	= 38 measures.	40 measures	= 115 measures.
15 measures	= 52 measures.	60 measures	= 155 measures.
20 measures	= 67 measures.		

This action then proceeds in a gradually decreasing ratio.

These very diversified experiments have put to a rigid test the truth of Berthollet's view. Whatever were the circumstances under which the reactions were tried, they invariably showed that the results were dependent both upon the nature and upon the quantity of all the substances in solution.

FERRIC GALLATE.

A solution of gallic acid was made of known strength. Equal portions of it were added to equal portions of the different ferric salts.

1 equivalent ferric nitrate with 1 equivalent gallic acid gave 100 parts of black salt.

1 equivalent ferric chloride with 1 equivalent gallic acid gave 88 parts of black salt.

1 equivalent ferric sulphate with 1 equivalent gallic acid gave 70 parts of black salt.

1 equivalent ferric citrate with 1 equivalent gallic acid gave 10? parts of black salt.

The mixture containing the citrate could not be accurately compared on account of its greenish hue. That made from the acetate was of an intense blue.

When single equivalents of nitrate of iron and gallic acid were mixed, a solution resulted in which the gallic acid had to such an extent combined with the sesquioxide of iron, that the addition of several equivalents of either one of the constituent substances caused a scarcely perceptible increase of colour.

The ferric chloride was then tried.

Ferric chloride.	Gallic acid.	Black salt produced.	Ferric chloride.	Gallic acid.	Black salt produced.
1 equiv.	+ 1 equiv.	88	1 equiv.	+ 4 equivs.	128
1 equiv.	+ 2 equivs.	108	1 equiv.	+ 6 equivs.	133
1 equiv.	+ 3 equivs.	120			

The citrate afforded a better opportunity of obtaining a numerical result representing the influence of the mass of one of the constituents.

Ferric citrate.	Gallic acid.	Black salt produced.	Ferric citrate.	Gallic acid.	Black salt produced.
1 equiv. +	5 equivs.	155	1 equiv. +	13 equivs.	297
1 equiv. +	7 equivs.	200	1 equiv. +	17 equivs.	353
1 equiv. +	9 equivs.	237	1 equiv. +	25 equivs	445
1 equiv. +	11 equivs.	270	1 equiv. +	33 equivs.	509

Experiments were also tried with gallate of potash in the place of gallic acid.

1 eq. fer. nit. + 1 eq. gal. of pot. gave 100 parts of black salt.
1 eq. fer. chl. + 1 eq. gal. of pot. gave 97 parts of black salt.
1 eq. fer. sulph. + 1 eq. gal. of pot. gave 68 parts of black salt.
1 eq. fer. citr. + 1 eq. gal. of pot. gave a blue solution.
1 eq. fer. acet. + 1 eq. gal. of pot. gave a precipitate.

A mixture of single equivalents of gallate of potash and ferric nitrate gave nearly, but apparently not quite, the same depth of colour as when an equivalent of gallic acid was mixed with the same iron salt.

Ferric gallate was prepared by dissolving the hydrated sesquioxide of iron in gallic acid. It was divided into two equal parts, to one of which successive portions of hydrochloric acid were added, while the other was diluted after each addition till it had been reduced to the colour of the acid mixture.

Hydrochloric acid added.	Water added to comparative solution.	Hydrochloric acid added.	Water added to comparative solution.
1 measure	= 3·4 measures.	3·25 measures	= 10·1 measures.
2 measures	= 6·6 measures.	4·5 measures	= 12·0 measures.

It requires no further experiments to show that the ferric gallate bears the same testimony as the sulphocyanide.

FERRIC MECONATE.

Similar experiments were made with meconic acid and the iron salts. After mixing these substances, it was found necessary to

allow the solutions to stand a minute or two before observation, in order that the full colour might be developed.

1 eq. ferric nitrate + 1 eq. meconic acid (3HO, C_{14} H_4 O_{14}) gave 100 parts of red salt.

1 eq. ferric chloride + 1 eq. meconic acid (3HO, C_{14} H_4 O_{14}) gave 96 parts of red salt.

1 eq. ferric sulphate + 1 eq. meconic acid (3HO, C_{14} H_4 O_{14}) gave 72 parts of red salt.

1 eq. ferric citrate + 1 eq. meconic acid (3HO, C_{14} H_4 O_{14}) gave 42 parts of red salt.

1 eq. ferric acetate + 1 eq. meconic acid (3HO, C_{14} H_4 O_{14}) gave a red precipitate.

The influence of successive additions of meconic acid to a mixture of single equivalents of that substance and ferric nitrate was tried.

Ferric nitrate.	Meconic acid.	Red salt produced.	Ferric nitrate.	Meconic acid.	Red salt produced.
1 equiv.	+ 1 equiv.	88	1 equiv.	+ 4 equivs.	75
1 equiv.	+ 2 equivs.	80	1 equiv.	+ 6 equivs.	73
1 equiv.	+ 3 equivs.	76	1 equiv.	+ 8 equivs.	74

Here, instead of finding an increase of colour, as might have been expected by analogy, there is a distinct though small decrease. On examining the action more fully, and by repeated experiments, it was found that the maximum colour was obtained when the ferric nitrate and the meconic acid were mixed in single equivalents (or rather, in the proportion of 12 atoms of the former to 11 of the latter); that the addition of more ferric nitrate to such a mixture did not notably increase the colour; that the addition to it of 0·25 equivalent of meconic acid made little change; and that a greater addition caused a decided diminution of the tint.

A mixture of one equivalent of meconic acid with one equivalent of sesquichloride of iron was examined in a similar manner. The addition of meconic acid was found in this case also to diminish the colour. The effect of successive additions of the ferric salt was more particularly tried.

Meconic acid.	Ferric chloride.	Red salt produced.	Meconic acid.	Ferric chloride.	Red salt produced.
1 equiv.	+ 1 equiv.	88	1 equiv.	+ 5 equivs.	99
1 equiv.	+ 1·2 equiv.	96	1 equiv.	+ 7 equivs.	93
1 equiv.	+ 1·8 equiv.	108	1 equiv.	+ 9 equivs.	99
1 equiv.	+ 2·6 equivs.	118	1 equiv.	+ 13 equivs.	119
1 equiv.	+ 3·8 equivs.	106			

It is evident that there is some action which twice changes the order of this series.

When ferric sulphate and meconic acid are mixed, it requires about seven atoms of the former to five of the latter to produce the greatest intensity of colour. It then just about equals in tint the mixture of five atoms of the ferric nitrate with the same amount of meconic acid, and made up to the same volume.

No amount of ferric citrate added to the above-mentioned amount of meconic acid is capable of bringing the colour up to that of the former mixtures.

These experiments were repeated with meconate of potash instead of the acid.

1 eq. fer. nitrate + 3KO, C_{14} H_4 O_{14} gave 100 parts of red salt.
1 eq. fer. chloride + 3KO, C_{14} H_4 O_{14} gave 73 parts of red salt.
1 eq. fer. sulphate + 3KO, C_{14} H_4 O_{14} gave 84 parts of red salt.
1 eq. fer. citrate + 3KO, C_{14} H_4 O_{14} gave a trace of red salt.
1 eq. fer. acetate + 3KO, C_{14} H_4 O_{14} gave a red precipitate.

These proportions differ considerably from those observed where meconic acid itself was employed.

The effect of successive additions of meconate of potash to the ferric nitrate was also tried.

Ferric nitrate.	Meconate of potash.	Red salt produced.	Ferric nitrate.	Meconate of potash.	Red salt produced.
1 equiv.	+ 0·33 equiv.	34	1 equiv.	+ 1 equiv.	88
1 equiv.	+ 0·5 equiv.	50	1 equiv.	+ 1·2 equiv.	84
1 equiv.	+ 0·8 equiv.	74	1 equiv.	+ 1·5 equiv.	69

Here the greatest intensity of colour evidently occurs when about single equivalents are mixed, the addition of a larger quantity of meconate of potash producing a rapid diminution of the colour.

The same was observed in respect to the ferric chloride. When single equivalents had been mixed, the addition of more ferric salt was not found to make any great difference in colour. This action, however, was examined quantitatively by means of the citrate.

Meconate of potash.	Ferric citrate.	Red salt produced.	Meconate of potash.	Ferric citrate.	Red salt produced.
1 equiv.	+ 0·8 equiv.	97	1 equiv.	+ 3·8 equivs.	102
1 equiv.	+ 1·2 equiv.	80	1 equiv.	+ 5 equivs.	125
1 equiv.	+ 1·8 equiv.	69	1 equiv.	+ 7 equivs.	154
1 equiv.	+ 2·6 equivs.	74	1 equiv.	+ 9·2 equivs.	165

Imagining that the rapid decrease of colour manifested when meconate of potash was added in excess to the ferric salt, might be due to the formation of some paler double compound, I added the potash salt to a solution of pure meconate. The colour was greatly diminished.

These results show satisfactorily enough that the amount of meconate of iron formed depends upon the nature of the various substances in solution; but their testimony in respect to the mass of these substances is obscured by the formation of these double compounds. Thinking to avoid this by always using the same amount of meconic acid and iron, and yet to exhibit the effect of mass, the following experiments were performed. Pure meconate of iron was treated with acetate of potash; it was quickly reduced to a pale yellow. Oxalate or phosphate of potash had the same effect. A strong solution of sulphate of soda was tried: —

Sulphate of soda added.	Water added to comparative solution.	Sulphate of soda added.	Water added to comparative solution.
5 measures	= 16 measures.	40 measures	= 58 measures.
10 measures	= 26 measures.	60 measures	= 80 measures.
20 measures	= 36 measures.		

Another solution of meconate of iron was similarly treated with dilute hydrochloric acid: —

Hydrochloric acid added.	Water added to comparative solution.	Hydrochloric acid added.	Water added to comparative solution.
2 measures =	3·6 measures.	7 measures =	15 measures.
3 measures =	5 measures.	9 measures =	20 measures.
5 measures =	10 measures.		

It is evident, that although a reduction of the amount of ferric meconate always takes place, there is some cause interfering with the regularity of the decrease of colour.

The amount of ferric meconate depends, therefore, upon the nature and upon the quantity of all the substances present at the same time in the solution; but the regularity of the action of mass, which was observed with the sulphocyanide and gallate, is not confirmed in this instance.

FERRIC PYROMECONATE.

Thinking that the irregularity in the influence of mass might be more or less connected with the tribasic character of meconic acid, it occurred to me that an examination of ferric pyromeconate would be desirable, since pyromeconic acid is monobasic, and yet strikes an intense red with the sesquioxide of iron, and in many other respects resembles the substance from which it is derived.

1 equivalent ferric nitrate + 3 equivalents pyromeconic acid gave 100 parts of red salt.

1 equivalent ferric chloride + 3 equivalents pyromeconic acid gave 86 parts of red salt.

1 equivalent ferric sulphate + 3 equivalents pyromeconic acid gave 39 parts of red salt.

1 equivalent ferric citrate + 3 equivalents pyromeconic acid gave 27 parts of red salt.

1 equivalent ferric acetate + 3 equivalents pyromeconic acid gave a red precipitate.

1 equivalent ferric nitrate + 3 equivs. pyromeconate of potash gave 100 parts of red salt.

1 equivalent ferric chloride + 3 equivs. pyromeconate of potash gave 74 parts of red salt.

1 equivalent ferric sulphate + 3 equivs. pyromeconate of potash gave 36 parts of red salt.

1 equivalent ferric citrate + 3 equivs. pyromeconate of potash gave 26 parts of red salt.

1 equivalent ferric acetate + 3 equivs. pyromeconate of potash gave a red precipitate.

On trying the influence of mass, it was found that the addition of pyromeconic acid rapidly *diminished* the colour of ferric pyromeconate; and that the colour was the deepest when the base was in large excess.

Thinking that the effect of a colourless salt upon the red pyromeconate might display more clearly the influence of mass, a mixture of ferric chloride and pyromeconic acid was experimented on with a solution of sulphate of potash: —

Sulphate of potash added.	Water added to comparative solution.	Sulphate of potash added.	Water added to comparative solution.
3·7 measures	= 12·5 measures.	20 measures	= 37·5 measures.
11·2 measures	= 27·5 measures.	30 measures	= 47·5 measures.

The monobasic pyromeconate appears, therefore, to be similar in its testimony to the tribasic meconate.

FERRIC ACETATE.

Twelve equivalents of acetate of potash were added to one equivalent of each of the ferric salts, and gave the following proportions: —

1 equivalent ferric nitrate + 12 equivalents acetate of potash gave 100 parts of red salt.

1 equivalent ferric chloride + 12 equivalents acetate of potash gave 139 parts of red salt.

1 equivalent ferric sulphate + 12 equivalents acetate of potash gave 112 parts of red salt.

1 equivalent ferric citrate + 12 equivalents acetate of potash gave no red salt.

These proportions differ greatly from those which have been previously observed.

The effect of successive additions of acetate of potash was tried:—

Ferric nitrate.	Acetate of potash.	Red salt produced.	Ferric nitrate.	Acetate of potash.	Red salt produced.
1 equiv.	+ 3 equivs.	88	1 equiv.	+ 21 equivs.	87
1 equiv.	+ 6 equivs.	109	1 equiv.	+ 30 equivs.	64
1 equiv.	+ 9 equivs.	109	1 equiv.	+ 39 equivs.	61
1 equiv.	+ 12 equivs.	102	1 equiv.	+ 48 equivs.	52
1 equiv.	+ 15 equivs.	96	1 equiv.	+ 63 equivs.	46

Here, again, as in the case of the meconate, there is something producing a great irregularity of action.

To a mixture of one equivalent of ferric nitrate, and three of acetate of potash, successive portions of the iron salt were added. They rendered the mixture much paler, reducing it at last almost to the colour of the nitrate itself.

In order to ascertain whether these changes of colour were due to the formation of double salts containing both iron and potash, three equal portions of the ferric acetate employed in the previous experiments were treated respectively with solutions of acetate of potash, acetic acid, and water. The potash salt caused a slight *increase* of colour, and the pure acid a great *decrease*, as compared with the effect of mere dilution. It is clear that there exist different combinations of acetic acid and sesquioxide of iron; indeed, it has been observed before by others, that a highly coloured solution of ferric acetate will spontaneously deposit red oxide and become almost colourless.

The ferric acetate, then, confirms Berthollet's view, but, like the meconate, its testimony in respect to the influence of the mass is equivocal.

FERRIC FERROCYANIDE.

The ferric ferrocyanide, although insoluble in pure water, is soluble in the presence of oxalic acid, giving a deep blue. A mixture was made of a known amount of ferrocyanide of potassium with that acid, and it was added to the various ferric salts. The blue from the nitrate, chloride, or sulphate was very intense; the mixture containing the acetate was colourless the first minute, but gradually became blue; while that containing the citrate also deepened in tint on standing. After remaining about two hours, the coloured mixtures were in the following proportions: —

1 equiv. ferric nitrate + 3 equivs. ferrocyanide of potassium gave 100 parts of blue salt.
1 equiv. ferric chloride + 3 equivs. ferrocyanide of potassium gave 87 parts of blue salt.
1 equiv. ferric sulphate + 3 equivs. ferrocyanide of potassium gave 89 parts of blue salt.
1 equiv. ferric acetate + 3 equivs. ferrocyanide of potassium gave 45 parts of blue salt.
1 equiv. ferric citrate + 3 equivs. ferrocyanide of potassium gave 60 parts of blue salt.

The effect of mass was also tried. The addition of more ferrocyanide of potassium to a mixture of one equivalent of ferric

nitrate and three of the ferrocyanide produced no appreciable increase of colour. With the citrate, however, the following numerical results were obtained:—

Ferric citrate.	Ferrocyanide of potassium.	Blue salt produced.	Ferric citrate.	Ferrocyanide of potassium.	Blue salt produced.
1 equiv.	+ 3 equivs.	88	1 equiv.	+ 9 equivs.	113
1 equiv.	+ 6 equivs.	107	1 equiv.	+ 15 equivs.	120

Acetate or citrate of potash added to a mixture of ferric nitrate and ferrocyanide of potassium in oxalic acid, produces no perceptible change at the moment of mixing; but a decrease of colour becomes apparent after a few minutes, and continues, becoming more and more marked for some hours.

The ferrocyanide then bears a similar testimony to the truth of Berthollet's position to what the ferric sulphocyanide and gallate do.

FERRIC COMENAMATE.

Single equivalents of comenamic acid ($C_{12}H_5NO_8+4HO$) were mixed with single equivalents of the different ferric salts. With the nitrate, chloride, and sulphate it gave a most intense purple, with the citrate a wine-red solution, and with the acetate a precipitate.

The three purple solutions were about equally deep in colour; they were unaffected by the addition of any amount of iron salt, but were reddened by the addition of comenamic acid. The mixture containing the citrate was uninfluenced in the character of the tint, and almost so in the depth of it, by the addition of any amount of either the acid or the iron salt. It was quite evident from this, that comenamic acid has a great tendency to combine with sesquioxide of iron in place of water, and that it is capable of forming two distinct compounds. Indeed, it was found that one equivalent, or less, of comenamic acid uniformly gave with one equivalent of nitrate of iron a deep bluish-purple compound; and that two equivalents, or more, gave a wine-red compound; whilst any proportion intermediate between one and two equivalents gave an intermediate tint.

Comenamate of potash and of ammonia gave similar results to comenamic acid itself; but the colour produced with the citrate at least was not so deep. The following were the ratios:—

1 equivalent ferric citrate + 1 equivalent comenamic acid gave 5 parts of red salt.

1 equivalent ferric citrate + 1 equivalent comen. of ammonia gave 4 parts of red salt.
1 equivalent ferric citrate + 1 equivalent comen. of potash gave 2·9 parts of red salt.

The addition of citrate of iron to a mixture of single equivalents of it and comenamate of potash caused an increase of colour, but no amount turned the solution purple.

Comenamic acid, then, is able to overcome the great affinity of citric acid for ferric oxide only so far as to produce the more acid salt. The purple comenamate was reddened instantly by citrate of potash, yet a large addition of that substance did not wholly destroy the colour.

That comenamic acid has not so great an affinity for sesquioxide of iron as to be unaffected by the presence of nitric, hydrochloric, or sulphuric acid, was easily demonstrated. The following experiment illustrates the action of such a substance. To a solution consisting of single equivalents of ferric chloride and comenamic acid, successive portions of hydrochloric acid were added. The original mixture was bluish-purple.

Hydrochloric acid added.	Colour of mixture.
3 measures.	Bluish purple, but paler by an amount equiv. to 25 measures of water.
6 measures.	Bluish purple, but paler by an amount equiv. to 40 measures of water.
9 measures.	Bluish purple, but paler by an amount equiv. to 54 measures of water.
15 measures.	Visibly redder, and paler by an amount equiv. to 80? measures of water.
21 measures.	Red purple.
31 measures.	Pink.
55 measures.	Still perceptibly pink.

The affinity, then, of comenamic acid for sesquioxide of iron, though very great, is influenced both by the nature and by the quantity of other substances present in the same solution.

FERRIC BROMIDE.

Experiments were also made on the ferric bromide. The iron salts were employed without dilution, as the bromide itself is but little redder than the chloride. Three equivalents of hydrobromic

acid added to one of ferric nitrate produced a distinct red; added to the ferric citrate, they produced little change in the colour. Yet the bromine has evidently a great tendency to combine with the iron; for, though the addition of a larger quantity of hydrobromic acid to the nitrate did perceptibly increase the colour, a maximum effect seemed attained when only about twelve equivalents were added. The addition of twelve equivalents in the case of the citrate produced likewise a red tint similar to that from the nitrate. Bromide of potassium did not redden the ferric citrate. Numerical results could not be obtained on account of the paleness of the colour.

THE FERRIC SALTS IN GENERAL.

Effect of mass of solvent.—In connection with these experiments on ferric salts, it became a matter of interest to ascertain whether changes in the mass of water itself had any influence on the composition of the salts contained in these coloured solutions.

The only methods which occurred to me of obtaining an answer to this inquiry, were, to ascertain whether dilution caused any greater or less decrease of colour in some substances than in others of the same tint; and whether the decrease of colour by dilution was uniform in the same salt, by whatever mixture it might be produced.

It has frequently been noticed that a red solution of ferric sulphocyanide is reduced by the addition of water more than the simple dilution seemed capable of accounting for, and more than the red meconate is.

To ascertain whether this is really the case, two solutions, the one of ferric sulphocyanide, the other of ferric meconate, were made up to the same depth of colour and the same volume, each occupying 200 grain measures; they were then equally diluted:

200 gr. m. of the sulphocyanide	equalled in colour	200 gr. m. of the meconate.
400 gr. m. of the sulphocyanide	equalled in colour	730 gr. m. of the meconate.
720 gr. m. of the sulphocyanide	equalled in colour	2460 gr. m. of the meconate.
1440 gr. m. of the sulphocyanide	equalled in colour	7540 gr. m. of the meconate.

The disparity here is very great, and takes place at an increasing ratio.

It seemed desirable to test, if possible, whether this diversity was due entirely to the sulphocyanide, or whether the meconate

might not also be departing from the ratio of decrease in colour which mere dilution would cause. For this purpose, five solutions were taken of equal bulk and of the same depth of colour. They consisted respectively of meconate of iron, a mixture of ferric chloride and sulphocyanide of potassium, port wine and water, red ink, and infusion of cochineal. These solutions, though not identical in colour, were sufficiently near for the purpose. On repeated dilution of each with equal amounts of water, they all retained the same colour relatively, except the sulphocyanide, which became yellowish and much lighter.

It may fairly be concluded, then, without predicting anything as to the action of water on dry salts, that large quantities of water have no specific action on meconate of iron, but that in some way they affect the sulphocyanide. Is this a mere physical effect upon the particular colour; or does some change take place in the composition of the salt itself? In order to test whether this action of water was influenced by the presence of other substances, red solutions of equal volume and equal depth of colour were prepared by the following admixtures:—ferric chloride with sulphocyanide of potassium in large excess; sulphocyanide of potassium with ferric chloride in large excess; ferric nitrate with sulphocyanide of potassium; the same salts with the addition of a large quantity of sulphate of potash; sulphocyanide of potassium with ferric acetate; ferrous and ferric sulphocyanide with sulphocyanide of lead; and nearly pure sesquisulphocyanide of iron. On repeated dilution with equal amounts of water, these all appeared to retain the same relative colour.

It seems, then, as far as this experiment can prove it, that the action of water, whatever it be, is exerted equally upon red sulphocyanide of iron, with whatever other substance it may be mixed. This removes any doubt that might have rested from this cause on some of the original experiments with ferric sulphocyanide: and the fact that those experiments were always comparative, leaves little ground for any possible objection.

An experiment was likewise tried in order to determine whether the presence of other substances had any influence in the dilution of meconate of iron. Solutions were taken of pure ferric meconate, and of mixtures of ferric chloride with meconic acid; of the same with meconate of potash, both in large excess and otherwise; of ferric nitrate with meconic acid; of the same with meconate of potash; and of ferric citrate with meconic acid. On repeated dilution with equal amounts of water, no notable difference was observed in the relative depths of colour of these several solutions, except in the case of the citrate, which, on standing for some hours after dilution, lost colour considerably. The red also was of a more pure crimson where there was nitric acid.

Pyromeconate of iron prepared by double decomposition was affected in colour by dilution in a similar manner to the meconate. Water, too, seemed to have the same effect on the blue ferrocyanide as on ammoniacal sulphate of copper. In these cases, however, the salts compared were not of precisely the same tint.

Relative strength of affinity. — Having considered the evidence borne by eight coloured and soluble ferric salts as to the truth of certain views of the laws that regulate chemical combination, we have found their testimony on the main points uniform. We may now go further, and by examining the results above given determine the relative degree of affinity exerted by the different acids for sesquioxide of iron as compared with potash.

The following is the order of affinity of the different acids experimented with for sesquioxide of iron and an equivalent amount of potash:—

Least affinity for sesquioxide of iron as compared with potash.

Hydrosulphocyanic acid	1
Nitric acid	4
Hydrochloric acid	5
Sulphuric acid	7
Gallic acid	10?
Pyromeconic acid?	
Meconic acid?	
Acetic acid	20?
Hydrobromic acid	
Comenamic acid	
Citric acid	100
Hydroferrocyanic acid	170?

Greatest affinity for sesquioxide of iron as compared with potash.

The numbers in the preceding table are deduced from the experimental data, but they must be considered as only rough approximations to the truth. The notes of interrogation indicate that the means of determination were themselves open to doubt.

Effect of differences of temperature. — The experiments narrated in this paper were all performed at the ordinary temperature. The slight changes that may have taken place in that respect from one day to another were incapable of affecting visibly the coloured solutions. Much greater variations had a perceptible effect, but whether this ever arose from changes in the balance of affinities I am not prepared to say.

I now pass on to consider the testimony borne by other coloured salts, not ferric compounds, in respect to the question at issue.

GOLD SALTS.

The bromide of gold is of an intense scarlet, whilst the chloride is of a yellow colour.

Pure chloride of gold free from hydrochloric acid was prepared. To a portion of this, three equivalents of bromide of potassium were added. The formation of the scarlet terbromide of gold was so complete, that the addition of either of the salts employed caused, singly, too small an increase of colour to be readily appreciated. Is it to be considered, then, that the decomposition in this case has been complete? may it be represented thus—

$$Au\ Cl_3 + 3K\ Br = Au\ Br_3 + 3K\ Cl?$$

This was more rigidly tested by adding chloride of potassium in large excess to bromide of gold.

Strong chloride of potassium added.	Water added to comparative solution.	Strong chloride of potassium added.	Water added to comparative solution.
5 measures	= 30 measures.	35 measures	= 105 measures.
10 measures	= 48 measures.	50 measures	= 135 measures.
20 measures	= 70 measures.	75 measures	= 180 measures.

Some difficulty was felt in determining the last numbers of this experiment, from the fact that the chloride of potassium had by its great excess converted nearly the whole of the bromide of gold into the yellow chloride, or still paler double chloride.

It was found that bromide of gold was reduced in colour by very small quantities of hydrochloric acid, or even of the common yellow crystals of the chloride of gold, which are, as is well known, the hydrochlorate of that salt.

These gold salts, then, have afforded a good example of the influence of mass in gradually counterbalancing and overcoming a strong affinity.

PLATINUM SALTS.

Neutral bichloride of platinum and different amounts of iodide of potassium were mixed in a series of vessels, diluted to an equality of bulk, and allowed to stand some hours for the colour to develop itself properly — a precaution which in this instance was necessary. The following were the appearances noted: —

Bichloride of platinum.	Iodide of potassium.	Character of mixture.
1 equiv. +	0·5 equiv.	Very pale brown solution.
1 equiv. +	1 equiv.	Reddish brown, and opalescent.
1 equiv. +	2 equivs.	The same, but deeper.
1 equiv. +	3 equivs.	The same; some biniodide of platinum deposited on the glass.
1 equiv. +	4 equivs.	Red; opalescence slight; biniodide of platinum deposited.
1 equiv. +	6 equivs.	Bright red; scarcely any opalescence or deposit.
1 equiv. +	8 equivs.	Brighter red; no opalescence or deposit.
1 equiv. +	10 equivs.	Still brighter red.
1 equiv. +	15 equivs.	Still brighter.

The formation of the insoluble iodide of platinum renders some of these cases less distinct in their testimony than the instances previously considered. The opalescence, too, was doubtless owing to a minute trace of solid matter. This, however, is perfectly clear, that the two salts, though they have mutually decomposed each other, have not done so in the atomic proportions; not according to the schemes

$$Pt\,Cl_2 + 2KI = Pt\,I_2 + 2KCl$$

and

$$Pt\,Cl_2 + 3KI = Pt\,I_2,\,KI + 2KCl.$$

It has required, in fact, about four equivalents of iodide of potassium to produce the maximum amount of the platinic iodide; and the latter terms of the series exhibit a still increasing amount of the intensely red double iodide of platinum and potassium. It may be expected that the double chloride is one of the salts produced in such a mixture. Successive additions of a strong solution of chloride of potassium to a mixture of one equivalent of bichloride of platinum with two of iodide of potassium, were found to reduce the colour greatly, making it browner.

COPPER SALTS.

Soluble copper salts are, I believe, all of a blue colour when dissolved in a large amount of water; but a strong solution of the chloride, and of one or two others, is green. It has frequently been observed, that on the addition of strong hydrochloric acid to a concentrated solution of sulphate of copper, a green colour takes the place of blue; and it has been naturally concluded that

chloride of copper was then formed. This reaction was likewise investigated.

Sulphate of copper.	Hydrochloric acid.	Colour of mixture.
1 equiv. +	1 equiv.	Blue.
1 equiv. +	2 equivs.	Blue, with a tinge of green.
1 equiv. +	3 equivs.	Dull green.
1 equiv. +	4 equivs.	Dull green.
1 equiv. +	6 equivs.	Bright green.
1 equiv. +	8 equivs.	Bright green.
1 equiv. +	16 equivs.	Very bright green.

From this it is evident that single equivalents of sulphate of copper and of hydrochloric acid are not resolved wholly (nor indeed to any great extent) into chloride of copper and sulphuric acid; and that the relative mass of the two substances influences the result.

In order to observe the influence of the mass of water, the following experiments were instituted. Eight portions were taken of a saturated solution of sulphate of copper at 60° F., and were mixed with progressively increasing amounts of strong hydrochloric acid solution. The colours produced were noted. They are given in column I. of the subjoined table. Each of the mixtures was then diluted with half its volume of water. The resulting shades are given in column II. Column III. represents the shades when the water was doubled; column IV. when the solutions were of three times their original volume: —

Sulph. cop. sol.	Hydroch ac. sol.	I.	II.	III.	IV.
50 mea. + 10	mea.	Perfectly blue.	Perfectly blue.	As Column II., but all paler and more blue.	Pure blue.
50 mea. + 12·5	mea.	Greenish blue.	Blue.		Pure blue.
50 mea. + 15	mea.	Distinctly green.	Blue, with trace of green.		Pure blue.
50 mea. + 20	mea.	Clear green.	Just a shade greener.		Pure blue.
50 mea. + 30	mea.	Bright green.	Dull bluish green.		Pure blue.
50 mea. + 40	mea.	Bright green.	Green		Blue, with a trace of green.
50 mea. + 50	mea.	Brighter green.	Green (Scarcely distinguishable.)		Blue, with a trace of green.
50 mea. + 70	mea.	Still brighter.	Green		Blue, with a trace of green.

It is not to be inferred that the sulphate of copper was in larger quantity in column IV. than in column I., for water acts according to its mass upon pure chloride of copper, converting it from green into a blue compound.

To seven portions of the standard solution of sulphate of copper, each measuring 50 parts, were added respectively 10, 20, 30, 40, 50, 70, and 100 parts of a saturated solution of chloride of sodium. There resulted a series of tints passing gradually from blue to almost pure green, without any sudden transition.

A strong solution of chloride of zinc added to a solution of sulphate of copper, also produced a greenish colour, which increased as more chloride was added.

Knowing the disposition of oxide of lead and acetic acid to combine, it occurred to me that chloride of lead might decompose the acetate of copper very readily. Accordingly, two equal portions of the blue acetate were mixed with equivalent amounts of chloride of lead and chloride of sodium in solution; and it was indeed found that the former caused a greater diminution of the colour than the latter did. In this experiment, much water was necessarily employed, but chloride of copper always gives a far paler blue solution than an equivalent amount of the acetate does.

These reactions with copper salts bear additional testimony, therefore, to the truth of the previous views.*

MOLYBDOUS SALTS.

As the molybdous fluoride gives a purple, and the chloride a green solution, these salts offered another means of testing whether complete or partial decomposition ensued on the mixing of binary compounds. Molybdous oxide was dissolved in hydrofluoric acid, and the resulting purple solution was treated with hydrochloric acid. It changed gradually to a greenish blue; and, on adding more hydrochloric acid, to a positive green. Time entered as an appreciable element into this change.

The converse of this experiment was also tried. The molybdous oxide dissolved in hydrochloric acid of a green colour. The addition of hydrofluoric acid to this gave at the first moment a rich

* After this paper had been read, the following note was added:—Changes in the state of combination of an element may be rendered visible by a change in the intensity of a colour, even where no change in its character occurs. Thus oxide of copper dissolved in acetic acid gi es a much more intense blue than when the same amount is dissolved in sulphuric acid. This fact was taken advantage of in the following experiment, which affords additional evidence of the truth of my main deduction. Sulphuric acid was added to a solution of acetate of copper; it reduced the colour greatly. The experiment was reversed, acetic acid being added to a solution of sulphate of copper; it deepened the colour, but considerable excess of the acid was required to make a very evident difference.

purple, which was immediately succeeded by a white precipitate, insoluble in any excess of hydrofluoric acid, but readily soluble in hydrochloric acid with reproduction of the green.

MANGANESE SALTS.

Intermediate between the protoxide of manganese and the non-basic oxides, there exists a brownish-red salifiable compound, of the formula Mn_3O_4. It is described in Gmelin's Handbook under the designation "manganoso-manganic oxide." Its solution in hot phosphoric acid or cold oil of vitriol is red, but it dissolves in other acids with a deep brown colour.

I prepared the sulphate and hydrochlorate of this base, and found that the addition of hydrochloric acid in excess caused a change in the colour of the sulphate from red to reddish brown, and eventually brown; while, on the other hand, the addition of sulphuric or phosphoric acid in excess to a solution of the brown chloride converted it into the red salt. Thus it appears that the oxide in question has no such affinity for either one of these acids, but that it is displaced more or less by the other.

BLUE GALLATE OF IRON.

Gallic acid, when added to iron salts, is apt to strike a deep blue colour, from the formation of a very stable compound of the organic acid with both the basic oxides of iron at once.

A blue solution was prepared by mixing solutions of gallic acid and of green vitriol that had been exposed to the air. The effect of sulphuric acid was tried.

Sulphuric acid added.	Water added to comparative solution.	Sulphuric acid added.	Water added to comparative solution.
1 measure	= 9 measures.	10 measures	= 63 measures.
2 measures	= 18 measures.	14 measures	= 105 measures.
4 measures	= 34 measures.	16 measures	= 136 measures.
6 measures	= 46 measures.	18 measures	= 174 measures.
8 measures	= 55 measures.	20 measures	= 204 measures.

This experiment suffices to prove the influence upon the production of this blue gallate, both of the nature and quantity of other substances present in the solution at the same time.

QUININE SALTS.

In his elaborate paper "On the Change of Refrangibility of Light,"* Professor Stokes has shown that various acid salts of quinine exhibit that remarkable internal dispersion of light which is now known by the name "fluorescence." He mentions the acid sulphate, phosphate, nitrate, acetate, citrate, tartrate, oxalate, and hydrocyanate, as giving rise to the phenomenon; while quinine dissolved in hydrochloric acid did not present any such appearance. He found, moreover, that the addition of hydrochloric acid, or chloride of sodium, to one of the fluorescent salts destroyed the colour. Hence he concluded, and no doubt correctly, that in these cases muriate of quinine was formed; and to obviate the objection that possibly the non-fluorescent salt in solution might be a sort of double salt, in which the quinine was combined with the hydrochloric and the other acid in atomic proportion, he devised the following elegant experiment. To a strong warm solution of neutral sulphate of quinine, which displays no fluorescence, a very small quantity of hydrochloric acid was added; it produced the blue appearance: more hydrochloric acid was added; the blue was destroyed. This seemed intelligible only on the supposition that the small quantity of acid first added displaced an equivalent amount of sulphuric acid, which, combining with the undecomposed sulphate, formed the acid salt which displays fluorescence to such a remarkable degree; and that the larger quantity of hydrochloric acid decomposed this again, setting free the sulphuric acid, and leaving the quinine in solution as hydrochlorate.

From the manner in which Professor Stokes describes and comments on these experiments, it is evident that he imagined (as most others would have done) that the decomposition was perfect, and that, in the particular experiment just mentioned, every particle of the quinine existed in the solution in the form of hydrochlorate, on account of the stronger affinity of that acid for the base. He states, moreover, that "even sulphuric acid is incapable of developing the blue colour in a solution of quinine in hydrochloric acid." If this be true, it evidently militates against the conclusions that double decomposition does not take place perfectly in solution, unless aided by the insolubility or volatility of one or more of the compounds produced, and that great mass counterbalances weak affinity. Accordingly, I repeated the experiments *quantitatively*, and performed some additional ones.†

* Philosophical Transactions, 1852.

† Since writing the above, my attention has been drawn to a paragraph in Professor Stokes's second paper (Philosophical Transactions for 1853, p. 394.), in which he remarks that the neutral hydrochlorate of quinine is not absolutely non-fluorescent, as first stated, and that the hydrocyanate is like the hydrochlorate.

Sulphate of quinine.	Hydrochloric acid.	Character of fluorescence.
1 equiv. +	0·5 equiv.	A deep blue entering far into the liquid.
1 equiv. +	1 equiv.	A more intense blue, and confined to the edges.
1 equiv. +	1·5 equiv.	Much as the preceding.
1 equiv. +	2 equivs.	Rather fainter blue.
1 equiv. +	3 equivs.	Decreasing.
1 equiv. +	4 equivs.	Still decreasing.
1 equiv. +	6 equivs.	Fainter.
1 equiv. +	8 equivs.	Still fainter.
1 equiv. +	12 equivs.	Very faint.
1 equiv. +	20 equivs.	Just visible.
1 equiv. +	30 equivs.	As above.
1 equiv. +	50 equivs.	Invisible except under the most favourable circumstances.

It will be seen at once, that the double decomposition between the sulphate of quinine and the hydrochloric acid was not perfect. Had it been so, the first line of the experiment would have been represented by the formula —

$$2(C_{44}H_{28}N_2O_4,\ HO,\ SO_3) + HCl = C_{44}H_{28}N_2O_4,\ HCl + C_{44}H_{28}N_2O_4,\ 2(HO,\ SO_3),$$

and the largest possible amount of fluorescence would have been obtained: while the second line would have been according to the formula —

$$C_{44}H_{28}N_2O_4,\ HO,\ SO_3 + HCl = C_{44}H_{28}N_2O_4,\ HCl + HO,\ SO_3,$$

and there would have been no fluorescence visible with this or any higher proportion of hydrochloric acid. But instead of single equivalents of sulphate of quinine and hydrochloric acid giving a non-fluorescent mixture, the blueness was only then attaining its maximum. Chloride of sodium was found to have even less power of decreasing the blue colour than an equivalent amount of the acid has.

Neutral hydrochlorate of quinine was prepared. Its solution diluted showed a mere trace of blue, which was removed on the addition of a drop or two of free hydrochloric acid. Portions of this solution were mixed with all the acids mentioned by Stokes as giving fluorescent compounds with quinine. The addition of

sulphuric, nitric, phosphoric, acetic or oxalic acid, instantly reproduced the blue colour in a very marked manner. Citric or tartaric acid added in very large excess also produced the blue, but it was faint. I failed to detect any change on the addition of a considerable amount of hydrocyanic acid.

Similarly, a solution of sulphate of soda in considerable excess was added to an acid solution of hydrochlorate of quinine. A very perceptible amount of blue made its appearance. This also is in perfect consonance with what might theoretically be expected, and indicates that not only had the commixture of sulphate of soda converted a portion of the hydrochlorate of quinine into sulphate, but the free hydrochloric acid had decomposed some of the sulphate of soda, liberating sulphuric acid, which had combined with the quinine salt to form the bisulphate. That a mixture of neutral sulphate of quinine with sulphate of soda does not give the blue tint, unless some free acid be added, was verified by previous experiment.

Stokes also states that iodide or bromide of potassium added to a solution of bisulphate of quinine, or the acid phosphate, destroys the fluorescence. On examining these reactions, I found that these haloid salts behaved precisely as the chloride did.

This accumulation of evidence all goes to prove that quinine follows the same laws as the substances previously considered.

COMPOUND ETHERS.

Compound ethers may be regarded as organic salts in which certain compound radicals take the place of metals, and it is to be expected that they will follow the same general laws as the binary compounds that have been previously examined. Their insolubility in water precludes the use of aqueous solutions of the substances intended to act upon them; but alcohol affords a convenient medium for the reaction; and when this is employed, results are obtained which are perfectly analogous to those already described in the case of different metallic salts. The following experiment may be taken as an example. A large excess of oxalic acid was dissolved in alcohol along with acetic ether, warmed, and allowed to stand for some hours. The mixture was then submitted to gentle distillation, and there passed over acetic ether mixed with alcohol and with oxalic ether. The oxalic acid had therefore displaced a certain amount of acetic acid; but though it existed in such large excess that it began to crystallise out, it had not displaced the whole.

GENERAL INFERENCES FROM THE PRECEDING EXPERIMENTS.

The concurrent testimony of the diversified experiments here detailed is in favour of the view, that when two binary compounds are mixed in solution, there ensues a partition of the two electro-positive between the two electro-negative elements, according to certain proportions regulated both by the difference of strength in the affinities, and by the relative quantities of the different bodies. The reverse of this does indeed appear at first sight to be the case in certain instances; as for instance when equivalent portions of sulphocyanide of potassium and ferric citrate are mixed, or of chloride of gold and bromide of potassium. But it makes all the difference whether there be a small, though inappreciable, quantity of the other salt formed at the same time, or whether the decomposition be absolute; and a consideration of the whole series of experiments, and of the influence of mass in these very instances, will leave, I think, a strong conviction on the mind that such cases differ from the others only in degree, and that if we possessed the means of observing minuter differences of colour we should find evidence of traces of the original salts still remaining. But of this each reader will form his independent judgment. Among those instances where evidently four salts were produced by the mixture of two, the following substances took part in the reaction:—

Iron (in both basic conditions), gold, platinum, mercury, copper, zinc, lead, molybdenum, manganese, baryta, lime, potash, soda, ammonia, hydrogen, ethyl, quinine.

Sulphuric, nitric, phosphoric, hydrochloric, hydrobromic, hydriodic, hydrofluoric, hydrosulphocyanic, hydroferrocyanic, acetic, oxalic, citric, tartaric, gallic, meconic, pyromeconic, and comenamic acids.

It must be borne in mind, that when, in studying the mutual action of AB and CD, we have determined the laws according to which A and D combine, we have equally ascertained them in reference to C and B; that is to say, to take a particular instance, if we find, on mixing ferric nitrate and sulphocyanide of potassium, that ferric sulphocyanide is formed in certain proportions according to the relative force of affinity and mass, we have determined this also in respect to the nitric acid and the potash. We know, indeed, that for every portion of ferric sulphocyanide produced, an exactly equivalent portion of nitrate of potash must be formed. And not only this, but in any such mixture, where we know the original amounts of the two salts, and the amount of any one of the four into which they are resolved, we have the data for determining the amounts of the other three likewise. Suppose (which is about the truth) that one equivalent of ferric nitrate mixed with

three equivalents of sulphocyanide of potassium produce one-fifth of an equivalent of ferric sulphocyanide, the following is the only formula which can represent the reaction. The amounts are multiplied by five to avoid decimals:

$$5(Fe_2O_3, 3NO_5)+15KS_2\,Cy=Fe_2, 3S_2\,Cy+12KS_2\,Cy +4(Fe_2O_3, 3NO_5)+3(KO, NO_5),$$

or more simply,

$$5AB+5CD=AD+4AB+4CD+CB.$$

Of course this method of reckoning is inapplicable where polybasic acids are concerned.

TESTIMONY FROM OTHER CHEMICAL PHENOMENA.

There are many chemical phenomena, beside those connected with colour, which bear testimony respecting the question whether two salts in solution resolve themselves into four.

The testimony of precipitation.—The idea that when double decomposition occurs, the acids and bases make a perfect exchange, arose doubtless from what is constantly observed when a precipitate ensues. In that case A combines wholly with D, and C with B. Yet this will be the inevitable result under the one theory as well as under the other. A mixture of single equivalents of nitrate of baryta and sulphate of potash may be taken as an illustration. Here, as has frequently been shown, if Berthollet's views be correct, at the first moment of mixing, a portion of the baryta combines with sulphuric acid, but that compound being insoluble is instantly put out of the field of action, and the resulting mixture really consists of nitrate of baryta, nitrate of potash, and sulphate of potash, which of course gives rise to a redistribution of the bases and acids, and a further production of insoluble sulphate of baryta, and so on, till the amount of nitrate of baryta remaining is infinitesimally small; while at the same time the whole of the potash must necessarily combine with the whole of the nitric acid. It is scarcely necessary to observe, that this division and precipitation will take place continuously until complete; and that it may be so rapid as to elude our notice.* The fact then that precipitation when it occurs is complete, decides nothing as to the relative merits of the two

* Yet it is easily conceivable that when the affinity for each other of the two substances that produce the insoluble compound is very weak, the action may last some time, and become evident to our senses. Is not this actually the case when sulphate of lime in solution is added to nitrate of strontia, or carbonate of soda to chloride of calcium, or an alkaline carbonate to tartrate of yttria, or oxalate of ammonia to sulphate of magnesia, &c. ?

theories of elective affinity. Yet there is an important difference to be noted. On Bergman's supposition, it can hardly be imagined but that cases will sometimes occur, where A has so strong an affinity for B, or C so powerful an attraction for D, that on mixing AB and CD, no interchange will take place, although AD may be an insoluble body. On Berthollet's supposition, the insoluble compound will always be wholly precipitated whenever by the interchange of acids and bases such a compound can be formed, even though it be against the preponderating direction of the affinities. Now this can be put at once to the test of experience: and what is the testimony of the thousands of double decompositions which chemists are in the habit of meeting with? Graham* says, "It is a general law to which there is no exception, that two soluble salts cannot be mixed without the occurrence of decomposition, if one of the products that may be formed is an insoluble salt." Gmelin†, even when arguing against Berthollet's views, admits the same fact, adding, "the only case which appears to present an exception is that observed by Th. Scherer‡, and this requires further examination." The case, which depends on the insolubility of oxalate of yttria, broke down on careful investigation.

It is then a law, without a single known exception, that if AB, CD, EF, &c., by any interchange of bases and acids, can possibly produce an insoluble substance, that insoluble compound does actually make its appearance. This seems to me almost conclusive evidence that the interchange always takes place originally to a greater or less degree; for I cannot believe, with one chemist of high repute, that "when bodies are brought into intimate contact, all the forces which exist, not only in themselves, but in all their possible compounds, are called into action at the same time," unless indeed it be by these compounds being actually formed.

The following experiments may illustrate more fully the truth of the explanation of complete precipitation which has been given above.

I. Strong solutions of sulphocyanide of potassium and ferric sulphate were mixed. The resulting intensely red liquid was divided into two equal parts. The one portion was largely diluted with water; and to the other portion a little strong alcohol was added, which caused the precipitation of sulphate of potash while ferric sulphocyanide was dissolved. The alcohol was poured off, and diluted with water till of the same volume as the first portion. It was far deeper in colour, indicating evidently that the insolubility of sulphate of potash in alcohol had removed it out of the sphere of action, and had caused a much larger proportion of

* Elements of Chemistry. † Handbook of Chemistry.
‡ Poggendorff, li. 470.

ferric sulphocyanide to be formed than would otherwise have been produced. Only a small quantity of alcohol was employed, and it was mixed with a large amount of water, in order to obviate as much as possible the objection that the same amount of ferric sulphocyanide might appear darker in alcoholic than in aqueous solution, which is indeed the fact.

II. Another red solution was prepared by mixing sulphocyanide of potassium and ferric sulphate, and it was divided into two equal portions. To one of these hydrochloric acid was added, which of course reduced the colour somewhat. To each was then added an equal portion of neutral phosphate of soda. The acid solution remained red, though paler than before; the neutral solution became colourless, and turbid, from the formation of a flocculent precipitate of ferric phosphate. That the insolubility of this salt in the neutral solution was the cause of the complete combination of the oxide of iron with the phosphoric acid, was further elucidated by adding phosphoric acid to the colourless mixture, which restored a faint red tint to the solution, doubtless because it had set free some of the sulphuric acid, which, redissolving the ferric phosphate, allowed of the formation of a small amount of the red sulphocyanide.

III. A mixture of three parts of ferric citrate, and four of ferrocyanide of potassium was prepared, and divided into two equal parts. To the one there was added a few drops of hydrochloric acid, to the other a few drops of oxalic acid. In the one case, the ferric ferrocyanide, being insoluble in hydrochloric acid, was precipitated, leaving no trace of iron in the solution; in the other case there was a blue solution, but the whole of the iron was not in the condition of ferric ferrocyanide, for the addition of more prussiate of potash caused it to become bluer. That this was due, not to the affinity of the oxalic acid for the ferric oxide, but to that of the citric acid, will be evident from the fact ascertained by the previous experiments on the ferrocyanide, that this result would not have been obtained had the nitrate been employed.

The testimony of volatilisation.—The argument that has been employed in the case of precipitation will apply, *mutatis mutandis*, with equal force in the case of volatilisation. I am not acquainted with any exceptional instance.

The testimony of crystallisation.—It will sometimes happen that certain quantities of AB and CD are mixed in an amount of water which is insufficient to keep in perfect solution AD, should the whole of A combine with the whole of D, although the salt itself is a soluble one. In such a case, if Bergman's view be correct, either no AD will form, however concentrated the solution, or, should double decomposition ensue, it will form to the fullest

extent possible, and may be expected to crystallise out at once with something like the rapidity with which precipitation usually takes place. If, however, Berthollet's theory be a true expression of the fact, a certain amount of AD will always be formed, but it may remain dissolved in the liquid, although if the whole of A had entered into combination with D it must have separated: yet, on concentration, AD will make its appearance; and should this, or anything else, determine the formation of crystals, or should they ensue on the primary mixing, the crystallisable salt is *pro tanto* put out of the field of action, and a redistribution of the acids and bases will take place with further crystallisation, until an equilibrium is obtained. Now the latter of these deductions describes what actually does take place, but there are several circumstances attending crystallisation from a mixture of salts which are not readily explained, and which I have as yet but imperfectly investigated.

The testimony of Malaguti's experiments.—Malaguti* examined the present question by taking two salts, both of which were soluble in water, but only one of which was soluble in alcohol, mixing them in equivalent proportions in water, and then pouring the aqueous solution into a large quantity of alcohol. Notwithstanding an objection recognised by the experimenter, three important results may be arrived at:—1st, that two salts on being mixed resolve themselves into four; 2nd, that this partition takes place in a definite manner; 3rd, that the proportions of the resulting salts are independent of the manner in which the different elements were originally combined.

The testimony of substances acted on by one of the compounds liberated in a mixture of salts.—It is to be expected that if two binary compounds be mixed, the formation of a new compound, though it remain in solution, may often be ascertained by certain chemical powers which it is capable of exerting. Instances of this are not wanting. Thus gold, as every one knows, is not attacked by hydrochloric or nitric acid singly, but is dissolved by a combination of the two; neutral potash salts of course have no action upon it; and yet gold dissolves readily in a mixture of either nitrate of potash and hydrochloric acid, or of chloride of potassium and nitric acid; whence it appears to me the conclusion may be fairly drawn, that in both mixtures the potash relinquishes a portion of the acid with which it was originally combined, or (which is the same thing) that it divides itself between the two.

Such experiments as this have no quantitative value, since the liberated substance immediately enters into a new combination,

* "Exposition de quelques faits relatifs à l'action réciproque des sels solubles," Ann. de Chim. et de Phys. 3, t. xxxvii. p. 198.

which must give rise to a fresh distribution of the different elements, and so on until no more of the active substance can be produced. A mere solvent action of the liberated body would be preferable to an action where positive chemical combination or decomposition takes place; but such cases scarcely exist. Among the actions which appear to answer this requirement most fully, is when a salt insoluble in water is dissolved in an acid, as, for instance, ferric phosphate in hydrochloric acid; yet even here a partial decomposition in all probability ensues. The only instructive numerical results which I have obtained were by mixing a saturated solution of oxalate of lime in hydrochloric acid with various proportions of acetate of potash or soda. The hydrochloric acid combining with the alkali caused a deposition of oxalate of lime, since that salt is not soluble in the acetic acid that was liberated at the same time.

Acetate of soda series.		Acetate of potash series.	
Salt added.	Oxalate of lime deposited.	Salt added.	Oxalate of lime deposited.
3 measures.	0·075 grm.	20 meas.	0·359 grm.
6 measures.	0·10 grm.	40 meas.	0·345 grm.
9 measures.	0·11 grm.	80 meas.	0·410 grm.
12 measures.	0·13·5 grm.	120 meas.	0·445 grm.
18 measures.	0·14·5 grm.	160 meas.	0·503 grm.
30 measures.	0·11 grm.	240 meas.	0·564 grm.
45 measures.	0·14·5 grm.		
90 measures.	0·19 grm.		

Notwithstanding certain irregularities in these series of numbers, it is sufficiently evident in both instances that the amount of oxalate deposited increased with the amount of acetate added, though not in direct ratio.

Supposed exceptions and limitations.—With this mass of evidence, and that of a very diversified character, the question arises,—Are we justified in concluding that the principles, which are so general, are *universal* in their application? Are there no exceptions? Is there no limitation?

As to exceptions, in the whole range of my experiments upon this subject, I have never met with a single instance of two substances having so strong an affinity for one another, that they combined to the exclusion of other bodies of like kind and present in the same solution, even if in large excess. Sometimes this rests not on demonstrative, but upon moral evidence, as, for instance,

when sulphocyanide of potassium and dissolved ferric ferrocyanide are mixed, where unquestionably the amount of ferric sulphocyanide produced must be quite inappreciable; yet that some is produced may be safely inferred I think from the fact, that sulphocyanide of potassium does give a red with the ferric acetate, and acetate of potash is capable of decomposing the ferric ferrocyanide to a well-marked extent.

During the controversy that ensued after the publication of Berthollet's treatise, many reactions were brought forward to prove the falsity of his views. Most of these were directed against certain positions of the French philosopher which were certainly untenable, while others were founded on a misapprehension of the question at issue. Those which appear the most formidable against the conclusions arrived at in this paper are, that boracic acid, or carbonic acid, or hydrosulphuric acid, is incapable of decomposing, in the least degree, sulphate of potash or any analogous salt; and that chloride of sodium is not affected at all by iodine. The proof of these statements rests in each instance upon the testimony of blue litmus paper. In the first case, the vegetable colour is not reddened; which is supposed to prove that no sulphuric acid has been liberated; yet if any had been set free there must have been formed at the same instant an equivalent amount of borate, or carbonate, or hydrosulphate of potash, each of which has an alkaline reaction, and would have restored the blue, or rather prevented the litmus from reddening. So in the case of the common salt and iodine (where by the way only one base is concerned), the chlorine, supposing it liberated, would not have bleached the litmus, but would have combined at the moment of its separation with some of the iodine present to form the terchloride of iodine which has a natural reaction. That very little decomposition does take place in these instances I have no doubt, but that there is actually none is not proved.

The action of water requires fuller investigation.

CONCLUSIONS.

The general conclusions arrived at in this paper may be summed up as follows:—

I. Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions.

II. These proportions are independent of the manner in which the different elements were originally combined.

III. These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture.

IV. An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

V. This equilibrium of affinities arranges itself in most cases in an inappreciably short space of time, but in certain instances the elements do not attain their final state of combination for hours, or even days.

VI. The phenomena that present themselves where precipitation, volatilisation, crystallisation, and perhaps other actions occur, are of an opposite character, simply because one of the substances is thus removed from the field of action, and the equilibrium that was first established is thus destroyed.

VII. There is consequently a fundamental error in all attempts to determine the relative strength of affinity by precipitation; in all methods of quantitative analysis founded on the colour of a solution in which colourless salts are also present; and in all conclusions as to what compounds exist in a solution drawn from such empirical rules as that "the strongest base combines with the strongest acid."

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V.—*Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre.*

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ALTHOUGH the exact determination of the commercial value of specimens of nitre may, for its importance, be ranked with the valuation of alkalies, manganese-ores, &c., and has, in consequence, occupied the attention of several chemists, it is certain that no method has hitherto been proposed which will enable the analyst to ascertain, with rapidity and precision, the amount of nitrate of potassa contained in any specimen of the saltpetre of commerce.

This assertion appears somewhat startling when it is remembered that several names of no mean authority are connected with the methods hitherto in use; but it exhibits the conclusion to which the authors have been conducted by a lengthened series of experiments, undertaken in the most perfect faith, not with the intention of shaking the foundations of the different methods of valuing nitre, but rather in order to convince themselves of the soundness of their pretensions to accuracy.

The manner in which this investigation originated is a sufficient proof of the disposition in which the authors commenced their experiments. Samples of nitre having been placed in their hands for very exact valuation, they had recourse to the process commonly

known as that of Pelouze, and were extremely surprised to find, that, with whatever care the experiments were conducted, the results obtained frequently exhibited great variations.

Various modifications of this process having been tried without success, the well-known method of deflagration was resorted to; but here, again, a very great uncertainty attended the experiments, so that an important discrepancy was often apparent in the results of several trials made upon the same sample.

It will be the object of this paper to describe the experiments which have been made upon these two methods, with the intention, firstly, of proving their title to confidence; secondly, of discovering the causes of inaccuracy; and thirdly, of ascertaining whether any modifications could be adopted which would still entitle them to a position among trustworthy analytical processes.

Before entering upon the experimental details, it may be deemed necessary to take a brief historical survey of the methods which have been employed at different times to ascertain the commercial value of saltpetre. These may be divided, with respect to the principles upon which they are founded, into mechanical and chemical methods.

The Swedish process of Swartz, which probably originated the term "refraction of saltpetre," consisted in an examination of the fracture of a cake of the fused salt, which could not certainly lead to any accurate numerical results.

A far more important mechanical method is that of Riffault, which appears to have been proposed in 1789, and has since been very generally used in the refineries of France. It consists in washing a weighed quantity of nitre with a saturated solution of the pure salt, and in determining the amount of the residue. The errors to which such a process must be liable are too obvious to need detailed consideration: they are chiefly attributable to the presence of chloride of sodium in the samples examined, and to the variations of temperature, which must depend upon the quantities of chlorides present; other objections of great weight at once suggest themselves to every practical chemist.

The Austrian method, proposed by Husz, consists in an exact determination of the temperature at which an aqueous solution of the sample begins to deposit crystals; but this is evidently liable to disturbance from the presence of chloride of sodium, and requires, moreover, greater delicacy of observation than should be necessary for a process to be carried on in a general chemical laboratory.

The authors have not considered it necessary to subject these

mechanical methods to any lengthened examination, believing that the opinion of chemists upon their inaccuracy is unanimous, and that their general adoption has been owing, not to their intrinsic merit, but to the want of more trustworthy processes.

There are only two well-known methods of valuing nitre, in general use, which are based upon chemical principles. The older method, usually known as that of Gay-Lussac, consists in converting the nitrate into carbonate of potassa, by deflagration with charcoal, the amount of the alkaline carbonate being afterwards determined by the alkalimeter.

The later process was introduced by Gossart,* and consists in ascertaining the amount of protoxide of iron converted into sesquioxide by a given weight of the sample of nitre. As originally proposed, a solution of protosulphate of iron, of known strength, was added to the acidified solution of nitre, until the presence of an excess of the protosalt could be discovered by ferricyanide of potassium, but experience had manifested the inaccuracy of this proceeding. Pelouze† modified it by dissolving a known weight of iron, converting a portion into sesquioxide by a given weight of the sample of nitre, and afterwards determining the unoxidised portion, by the method of Margueritte, with a standard solution of permanganate of potassa.

The following table contains the results of several trials of this method, conducted exactly according to the directions given by its author: —

TABLE I.

Exp.	Nitre.	Iron.	Iron unoxidised.	Nitre found.	Nitre per cent.
1‡.	18·53	31·00	0·85	18·12	99·40
2.	18·50		Gave a result somewhat higher.		
3.	20·10	30·00	0·75	17·58	87·46
4.	20·16	30·00	0·37	17·81	88·33
5.	20·05	30·00	0·41	17·78	88·67
6.	20·18	31·00	0·30	18·45	91·42
7.	20·26	33·50	0·30	19·95	98·48
8.	17·83	32·80	trace	19·71	110·55
9.	17·80	33·26	1·50	19·09	107·20
10.	17·64	32·46	0·30	19·33	109·50
11.	14·56	30·40	3·10	16·41	112·70

* Compt. rend. January 1847. † Ann. Ch. Phys. June 1847.

‡ Experiments 1 to 11 inclusive were made with the same sample of *crude* nitre.

TABLE I. (continued.)

Exp.	Nitre.	Iron.	Iron unoxidised.	Nitre found.	Nitre per cent.
12*.	15·00	35·12	10·25	15·12	100·80
13.	10·00	30·31	12·51	10·80	108·00
14.	18·00	32·64	3·08	17·97	99·83
15.	10·00	28·06	11·14	10·28	102·80
16.	19·00	33·57	1·95	19·22	101·05
17.	19·00	32·42	0·31	19·52	102·73
18.	19·00	32·83	1·04	19·32	101·68
19.	17·60	30·53	0·31	18·37	104·37

In most of these experiments, the iron was dissolved in concentrated hydrochloric acid, in a flask furnished with a cork and glass tube drawn out to a fine point. As soon as the metal had disappeared, the cork was withdrawn, the nitre washed in as quickly as possible, the cork replaced, and the solution boiled until the brown colour due to the nitric oxide had disappeared: it was then rinsed into a large flask, diluted with about 40 oz. of water, and the amount of iron left unoxidised was determined by means of a dilute solution of permanganate of potassa.

In Experiment 9, the nitre was dissolved in water and poured into the boiling solution while hydrogen was being evolved.

In Experiment 10, the solution of nitre was poured down a funnel tube, the extremity of which dipped into the acid solution of iron, a column of this solution having been made to ascend in the tube by a momentary closing of the egress tube, so that no air whatever was introduced.

In Experiment 11, the nitre was placed in a small bottle, which was suspended in the flask by a horsehair, and was only let down when the iron was completely dissolved; a layer of carbonate of soda was placed over the nitre, to prevent any premature contact with drops of the acid liquid.

In Experiment 12, the solution was boiled for half an hour after the introduction of the nitre; in Experiment 16, the boiling was continued for six minutes only; in Experiment 17, for twenty minutes; and in Experiment 18, the solution was boiled nearly to dryness.

An examination of this table leads to some curious inferences respecting the general working of the process.

The first experiment, in which the quantities employed were

* Experiments 12 to 19 were made with perfectly pure nitre.

almost exactly those recommended by Pelouze—viz. 2 grms. (30·9 grs.) of iron and 1·2 grm. (18·5 grs.) of nitre—furnished a result which might have been accepted with confidence had the sample of nitre been supposed nearly pure.

In the third, fourth, and fifth experiments, where the quantity of iron was diminished, and that of the nitre increased, the amount of nitre indicated by the oxidised iron fell very considerably; and between these three experiments, the quantities employed being nearly the same, no great discrepancy is observed.

When, however, as in the sixth and seventh experiments, the quantity of the iron is increased, though that of the nitre remains the same, a very considerably higher result is obtained.

In seeking for the cause of these variations, the attention of the authors was first directed to that adverted to by Pelouze—viz. the access of air to the solution containing the brown compound of the protosalt of iron with nitric oxide, the tendency of this solution to absorb oxygen being well known. The additional precautions taken to exclude air in the ninth and following experiments, had no effect in diminishing the error, which was, indeed, greater in these experiments than in those where no great precautions were adopted. The sixteenth and following experiments prove that the duration of the ebullition is also without effect upon the result.

In conducting these experiments, it was found difficult to hit the exact point at which the addition of the solution of permanganate of potassa should be discontinued; and since it was possible that this might give rise, in some degree, to the discrepancy in the results, a number of experiments were made, in which moderately diluted sulphuric acid was substituted for the hydrochloric, when no such difficulty was experienced, the colour of the sesquisulphate of iron being far lighter than that of the sesquichloride.

TABLE II.

Exp.	Nitre.	Iron.	Iron unoxidised.	Nitre found.	Nitre per cent.
1.	10·00	22·43	5·89	10·05	100·50
2.	10·00	20·00	3·46	10·05	100·50
3.	10·00	31·94	16·04	9·67	96·70
4.	6·00	21·43	10·91	6·39	106·50
5.	6·00	20·20	8·91	6·86	114·33
6.	6·00	20·05	9·51	6·40	106·66
7.	6·00	21·63	11·71	6·03	100·50
8.	10·00	32·14	15·91	9·87	98·70

TABLE II. (continued.)

Exp.	Nitre.	Iron.	Iron unoxidised.	Nitre found.	Nitre per cent.
9.	10·00	21·35	3·82	10·60	106·00
10.	10·00	30·18	13·73	10·00	100·00
11.	10·00	21·55	3·65	10·88	108·80
12.	15·00	32·20	6·22	15·79	105·26
13.	15·00	32·95	4·94	17·03	113·53
14.	18·00	30·49	0·51	18·53	102·94
15.	18·00	31·02	1·80	17·76	98·66
16.	18·00	31·13	1·69	17·90	99·44
17.	18·00	31·27	1·63	18·02	100·11
18.	18·30	31·49	1·30	18·35	100·27
19.	10·00	30·80	13·80	10·30	103·00
20.	18·30	31·16	2·10	17·77	97·10
21.	18·30	30·36	0·56	18·11	98·96

In these experiments some difficulty occasionally arose from the separation of an insoluble sulphate of sesquioxide of iron, which was only redissolved with considerable difficulty, and much interfered with the ebullition. In Experiments 5 and 13, the boiling was continued for a short time only, and the solution had still a brown tinge.

In Experiments 15, 16, and 17, the solution was boiled as long as possible; while in Experiment 18 it was boiled only for a short time.

It is apparent from this table, that, although the results obtained with sulphuric acid are generally more concordant than those obtained with hydrochloric acid, there is yet too great a variation observed in the results of several experiments, conducted as nearly as possible under the same conditions, to allow of any implicit confidence.

The results occasionally exhibited, both in this and in the preceding table, are sufficient to show that there is no want of correctness in the broad principle of the method, since several experiments in succession may furnish numbers agreeing very closely with each other. The cause of the remarkable variations occasionally observed must rather be sought for in some circumstance not directly connected with the theory of the operation.

Attention was therefore next directed to the discovery of some modification of the method which should so far diminish the frequency of the variations as to render it capable of application in commercial analysis.

Previously, however, to advancing in this branch of the inquiry, it was considered necessary to institute a few experiments in confirmation of the view generally taken respecting the action of nitric oxide upon the protosalts of iron.

5 grs. of iron were dissolved in hydrochloric acid, in a flask through which a stream of carbonic acid was passed in order to exclude air: when the iron was entirely dissolved, the flask was connected with an apparatus from which binoxide of nitrogen (prepared by the action of dilute nitric acid upon copper, and transmitted through water) was passed to complete saturation; the solution was then boiled while a stream of carbonic acid was passed through it, until all the binoxide of nitrogen was expelled. The solution of permanganate of potassa indicated 4·962 grs. of iron, showing that nitric oxide is without effect if air be excluded.

Three experiments with larger quantities of iron confirmed this result: —

Exp.	Iron employed.	Recovered.
1.	13·88	13·79
2.	15·08	15·00
3.	14·99	14·88

3 grs. of iron were dissolved in a similar manner, and, the solution having been saturated with nitric oxide, the cork and tubes were very rapidly withdrawn, replaced by a cork with a capillary tube, and the experiment terminated as usual; the permanganate of potassa then indicated only 1·602 grs. of unoxidised iron, nearly one-half of the protoxide having been converted into sesquioxide by the air admitted when the cork was changed.

Some experiments were then tried in which the solution, after saturation, was boiled only for five minutes in the stream of carbonic acid, when it was found that although the brown colour of the solution had changed to a light yellow, there must still have been a little nitric oxide left in the liquid when it was brought in contact with the air, since a considerable amount of iron had been peroxidised.

Exp.	Iron employed.	Iron recovered.
1.	14·96	13·75
2.	14·44	14·02
3.	13·35	13·22
4.	11·49	11·40

When the solution of protochloride of iron was saturated with

nitric oxide in a flask filled with carbonic acid, and the iron determined without boiling, an excess of the solution of permanganate of potassa was consumed.

Exp.	Iron employed.	Iron recovered (apparently).
1.	12·81	16·00
2.	12·85	14·40
3.	12·12	16·25

This result was explained when some nitric oxide was passed into water, in a flask filled with carbonic acid, and permanganate of potassa was afterwards added, when a rapid deoxidation took place, but only upon the surface.

The action of nitric oxide upon the acid solution of protosulphate of iron was then examined.

11·68 grs. of iron were dissolved in sulphuric acid, the solution saturated with nitric oxide, in a flask filled with carbonic acid, and the nitric oxide subsequently expelled by boiling the solution, when the stream of carbonic acid was rapidly passed; the permanganate of potassa then indicated 11·63 grs. of iron, proving that, if air be excluded, nitric oxide is without effect upon the solution.

Four experiments conducted in a similar manner, except that the stream of carbonic acid was not continued while the nitric oxide was being expelled, showed how slight an access of air can modify the result.

Exp.	Iron employed.	Iron recovered.
1.	13·76	13·47
2.	12·14	11·93
3.	11·04	10·45
4.	12·14	11·70.

In the following experiments, the solution was treated with binoxide of nitrogen in a flask filled with carbonic acid, the excess of the binoxide afterwards displaced by that gas, and the iron determined without boiling the solution.

Exp.	Iron employed.	Iron recovered.
1.	11·05	11·02
2.	11·93	11·91
3.	13·02	13·06
4.	12·03	12·04
5.	12·32	12·24

The difference cannot fail to be remarked between the results in these cases, and in the corresponding experiments with the hydrochloric solution,—a difference which may perhaps be explained by the circumstance that a more stable compound is formed by nitric oxide with the protosulphate than with the protochloride of iron, and therefore that, in the case of the sulphuric solution, the residual binoxide of nitrogen does not so readily undergo partial oxidation at the expense of the air, and thus become capable of reducing the permanganate. Some confirmation is afforded to this view by the circumstance that the expulsion of the nitric oxide from the sulphuric solution is far more gradual and difficult than when hydrochloric acid has been employed.

From these experiments it is quite evident that the binoxide of nitrogen is without effect upon the acid solutions of the protosalts of iron, if air be entirely excluded, but that unless the most rigid precautions are taken to ensure this, an oxidation of a part of the protoxide of iron is inevitable.

It then became necessary to endeavour to modify the process in such a manner as to preclude the possibility of an error from this cause.

The iron was dissolved in hydrochloric acid, in a flask filled with carbonic acid gas, and the nitre, having been suspended in a small tube, was let down into the solution when all the air had been expelled; in this case far too little nitre was obtained. Imagining that the deficiency might be due to the action of the vapour of hydrochloric acid upon the nitre, the latter was covered in the tube with a layer of bicarbonate of soda, but still a great deficiency was observed. In order to avoid any possibility of error from the rapid evolution of carbonic acid when the tube was allowed to fall into the liquid, a layer of borax was substituted for the bicarbonate, but only 93 parts for 100 of nitre were obtained.

In order to ascertain how far the loss might be due to the expulsion of nitric acid, as such, when the nitre came suddenly in contact with the boiling liquid, two experiments were made, in an apparatus filled with carbonic acid, the nitre being introduced only when the solution had quite cooled. The first gave 89, the second 94 per cent. of nitre in the pure salt.

A few of the experiments tried with every precaution to exclude air gave very accurate results, but the circumstances regulating these appeared to be so far beyond control, that it was impossible to obtain similar results from three or four experiments in succession, conducted with apparently equal care. The experiments were

varied by employing sulphuric instead of hydrochloric acid, but without any beneficial result.

With a view to ascertain how far the errors might be connected with the imperfect deoxidation of the nitric acid by the protosalt of iron, the following experiments were undertaken, in which the evolved gas was collected and examined.

22·93 grs. of iron were dissolved in dilute sulphuric acid (sp. gr. 1·3), and, as soon as all the air had been expelled, 14 grs. of nitre, contained in a small tube, were dropped into the liquid, the gas being collected over mercury: after the ebullition had been continued until the brown colour of the liquid had disappeared, the volume of gas was 11 cub. in.

2 cub. in. of this gas, exposed to the action of hydrate of potassa, did not diminish in volume.

2 cub. in., treated with solution of protosulphate of iron, left only 0·03 cub. in. unabsorbed; it therefore consists of nearly pure nitric oxide, the small unabsorbed portion being due probably to the residual air.

Theoretically, the 14 grs. of nitre should have yielded 12·98 cub. in. of nitric oxide.

The amount of nitre inferred from the determination of the unoxidised iron was only 86 per cent., while the 11 cub. in. of binoxide of nitrogen would represent 84 per cent., which is sufficient to show that the oxidation of the iron is attended with a *corresponding* evolution of that gas.

In a second experiment, the nitre was covered with a layer of borax, to prevent any loss of nitric acid from the spirting of the acid liquid into the bottle.

Iron employed	47·3	grs.
Nitre „	15·3	„
Total vol. of gas	12·75	cub. in.

which was proved, as before, to be pure nitric oxide.

Theoretically, 14·9 cub. in. of gas should have been obtained.

The amount of nitre corresponding to the iron oxidised was 90·6 per cent., while the 12·75 cub. in. of gas would represent 89·15 per cent. of nitre.

This affords a still closer confirmation of the general opinion respecting the action of nitre upon the acid solutions of protosalts of iron.

Two additional experiments exhibited the marked deficiency in the nitric oxide evolved.

Exp.	Iron.	Nitre.	Nitric oxide.	Nitre calculated from the nitric oxide.	
1.	20·81	12·17	10·89 cub. in.	11·74	96·46 p. c.
2.	42·07	17·54	13·17 „	14·09	80·33 „

The next question for consideration was, what became of the nitric acid not represented by the binoxide of nitrogen evolved? With reference to this point, an experiment was made in such a manner that the steam evolved while the nitre remained suspended in the flask could be passed into a solution of blue litmus. The latter was not perceptibly reddened, showing that no nitric acid was carried off in consequence of the accidental contact with drops of sulphuric acid before the salt was allowed to fall into the liquid.

Iron employed . . .	29·89 grs.
Nitre „	17·80 „
Nitric oxide	14·65 cub. in.

which correspond to only 15·68 grs. of nitre, or 88·09 per cent.

In the following experiment, the evolved gas was passed through a solution of pure carbonate of soda, which was afterwards evaporated to dryness. A portion of the residue, when treated with dilute sulphuric acid, evolved red fumes of nitrous acid: after boiling the liquid till no more red fumes were evolved, abundance of nitric acid was detected by the tests with indigo and sulphate of iron, showing that nitrous (and perhaps nitric) acid had escaped deoxidation.

Iron employed . . .	33·95 grs.
Nitre „ . . .	19·66 „
Nitric oxide (after removing the carbonic acid) . . .	13·52 cub. in.

corresponding to only 73·58 per cent. of nitre.

To prove that no error was caused by the method of suspending the nitre in this experiment, another was performed in the same manner, except that the tube containing the nitre was allowed to remain suspended above the surface of the boiling acid liquid, as usual, and not allowed to drop down: in this case no trace of nitrous or nitric acid was found in the solution of carbonate of soda.

In the next experiment, the tube containing the nitre was not suspended by a horsehair, but merely lodged on a cork shelf in the neck of the flask, so that it could be allowed to descend into the liquid by merely turning the flask,—thus preventing any error

which might be caused by the accidental admission of air while loosening the cork to disengage the horsehair.

45 grs. of iron and 20 of nitre were employed, and the gas was passed, as before, through a solution of carbonate of soda, which was afterwards found to contain little nitrous acid, but a considerable quantity of nitric acid. The solution remaining in the boiling-flask after the experiment was decomposed with carbonate of soda (previously tested for nitric acid) filtered from the iron precipitate, evaporated to dryness, treated with an excess of dilute sulphuric acid, which did not evolve any fumes of nitrous acid, afterwards mixed with a large quantity of concentrated sulphuric acid, and distilled. When a part of the liquid had distilled over, it was tested with solution of indigo, which indicated scarcely a trace of nitric acid, although this could be very readily detected in the contents of the retort. Moreover, no nitric acid could be found in the succeeding portions of the distillate, although the distillation was pushed to the utmost.

This observation possesses some importance in an analytical point of view, explaining, as it does, the inaccuracy (generally acknowledged) of the method of determining nitric acid in the nitrates by distilling with sulphuric acid, and proving the necessity for caution in testing for nitric acid by this method. Several experiments afforded full confirmation of the fact that nitric acid, and occasionally nitrous acid, could be found in the vapours evolved during the action of the nitre upon an acid solution containing a large excess of protosulphate of iron, and that the solution in the flask often contained a considerable quantity of undecomposed nitric acid.

It naturally excited great surprise that nitric acid should be capable of existing, though in relatively small quantity, in a solution of protosulphate of iron which contained a large excess of sulphuric acid, and had been boiled for a considerable time. Numerous experiments, however, made with the greatest care and with varying proportions, have perfectly convinced the authors of the fact. Judging from the experiment above mentioned, where the nitric acid could not be recovered by distillation, it would seem probable that this acid may be supposed to have remained in the solution in the form of undecomposed nitrate of potassa,—a supposition which is assuredly less preposterous than that it should exist in the free state.

It still remained to be proved whether the action of a hydrochloric solution was similar to that in which sulphuric acid was used.

The nitre was suspended, as usual, in a small tube, and covered with a layer of carbonate of soda; the evolved gas was passed into water excluded from air. This was found, after the experiment, to contain a very slight trace of nitric acid.

Iron employed	. .	35·67 grs.
Nitre „	. . .	15·00 „
Iron unoxidised	. .	11·23 „

indicating 99·06 per cent. of nitre.

The evolved gas consisted only of nitric oxide mixed with a little carbonic acid from the carbonate of soda.

No appreciable quantity of chloride of iron was found in the water through which the gas had been passed.

Another experiment was performed in a similar manner, the evolved gas being conducted through a solution of carbonate of soda, which was found to contain a trace of nitric acid after the experiment.

No nitric acid could be detected in the iron solution.

In a third experiment, with similar proportions, the gas was first passed into a small flask containing water (to absorb the hydrochloric acid), and then into a flask containing a considerable quantity of moistened carbonate of soda.*

The iron solution was decomposed by carbonate of soda, and carefully tested for nitric acid, but without result.

An experiment was then made in which the tube containing the nitre (covered with carbonate of soda) was allowed to slip down into the solution without loosening the cork.

In this case, also, abundance of nitric acid was found in the condensing flask.

Iron employed	. .	34·52 grs.
Nitre „	. . .	15·00 „
Iron unoxidised	. .	10·61 „

corresponding to 96·8 per cent.

To prove that the nitric acid was not accidentally carried over before the nitre was brought in contact with the iron solution, the last experiment was repeated, but without allowing the nitre to drop into the flask: in this case, although the ebullition was continued for an unusual period, no trace of nitric acid could be detected in the condensing flask.

* It is worthy of remark that in this case the water in the condensing-flask contained a very appreciable amount of iron. A small amount of nitric acid was also found in this flask, but a far larger quantity in that containing the carbonate of soda: no nitrous acid was detected.

In one experiment, a layer of quicklime was placed over the nitre, to prevent any loss of nitric acid due to the sudden evolution of carbonic acid from the carbonate of soda; but in this case only 95·6 per cent. of nitre was obtained, and a considerable quantity of nitric acid was found in the condensing-flask.

The most important conclusions which can be drawn from the experiments above detailed may be stated as follows:—

1. That the reaction upon which the method in question is founded is perfectly correct, and therefore it frequently happens that most accurate results are furnished by it; but

2. That these results are extremely liable to certain disturbing causes, which are so far beyond the control of the operator as to deprive the method of that certainty so essential to any process in use for commercial analysis.

3. That a very important source of error, in the ordinary mode of proceeding, is the absorption of oxygen from the air; and although the oxidation, through the intervention of the nitric oxide with which the flask is filled, may be prevented by simple arrangements, it is very difficult, especially when sulphuric acid is employed, to ensure the complete expulsion of the nitric oxide from the iron solution; and when the latter, containing still a little of this gas, is brought in contact, at a high temperature, with the air, oxidation immediately ensues, thus causing an apparent increase in the amount of nitre obtained. This source of error was adverted to by Pelouze in his original memoir.

4. That a variable quantity of nitric (and sometimes of nitrous) acid escapes unreduced, when nitrate of potassa is introduced into boiling acid solutions of protochloride or protosulphate of iron, even in large excess.

5. That when nitrate of potassa is introduced into a boiling solution of protosulphate of iron, containing a large excess of sulphuric acid, an appreciable quantity of nitric acid may remain in the solution, even after prolonged ebullition.

The authors next examined the method of Gay-Lussac.

Since, apart from other considerations, the accuracy of this process depends upon the degree of precision with which neutralisation is effected by means of an acid of known strength, it became necessary to institute some experiments for the purpose of determining the essential conditions for attaining this object.

The measure employed for the acid was a tube *burette*, of the form now generally in use, having a fine opening for delivering the

acid. This instrument was capable of containing 1000 grains of water, and was divided into 200 equal parts.

The different specimens of acid employed were so far diluted that a little less than 1000 grain-measures were required to neutralise the amount of carbonate of potassa corresponding to 20 grains of nitre. An acid of this description contains from 8· to 8·5 grains of SO_3 in 1000 grain-measures. The strength of the acid having been approximately ascertained by the neutralisation of a known weight of carbonate of soda, was finally determined with the greatest possible accuracy by precipitation as sulphate of baryta.

An aqueous infusion of litmus, free from alkali, was employed to colour the solution under examination, the same quantity being used in every case, so as to impart a rather deep blue colour to the liquid.

It was found, by several preliminary experiments, that the transition of the colour of the litmus was difficult to appreciate exactly, until the liberated carbonic acid had been expelled, on account of the wine-red tint which the latter imparted to the liquid. Experiments with pure carbonate of soda showed that no difference in the results was obtained, whether the carbonic acid was removed by exposure *in vacuo* or by ebullition. The most convenient method of proceeding is to add to the coloured alkaline liquid, contained in a flask, a sufficient quantity of acid to produce the wine-red tint; to heat the mixture to ebullition, adding a few drops of acid from time to time, until the peculiar onion-skin-red colour, imparted by the stronger acids to litmus, is obtained. The accurate appreciation of the colour is much facilitated by using, as a standard of comparison, a similar quantity of coloured water, to which a few drops of sulphuric acid have been added.

In the latter part of the present series of experiments, it was customary to continue the addition of the acid, drop by drop, to the solution, which was boiled after each addition, until it failed to produce in the liquid a cloud of a lighter colour. The observations were made by holding the flasks at a little distance over a sheet of white paper.

The lamp-black employed in the experiments left merely an inconsiderable amount of residue upon incineration. It was thoroughly ignited in a closed crucible before use. The chloride of sodium was perfectly pure, and carefully dried.

A number of experiments were first made with the proportions generally recommended in chemical works; namely, 1 part of lamp-black, 4 of nitre, and 24 of salt: 20 grains of nitre were

employed for most of the experiments. This was mixed with the lamp-black in a platinum crucible, with the aid of a glass rod. The chloride of sodium was then added, and a very intimate mixture effected in the same manner. The crucible was then covered and cautiously heated, so that deflagration might take place with moderate violence. It was afterwards heated to redness for two or three minutes. On cooling, the mass was thrown into a beaker, treated with hot water, the residual carbon filtered off and completely washed, and the alkalinity determined according to the manner above described.

TABLE III.

Exp.	Nitre found.	Nitre per cent.
1.	19·84	99·20
2.	19·95	99·75
3.	19·95	99·75
4.	19·74	98·70
5*.	18·74	93·70
6*.	18·89	94·45
7*.	19·34	96·70
8†.	15·77	93·80
9‡.	17·13	85·65
10.	19·86	99·29
11.	19·99	99·99
12.	19·09	95·45
13.	19·59	97·95
14.	19·59	97·95
15.	19·88	99·40
16‡.	17·66	88·30
17‡.	17·96	89·80
18.	19·79	98·95

In No. 7 the ingredients were very intimately mixed in a mortar, with a view of ascertaining whether the deficiency in former experiments might have arisen from imperfect mixture.

No. 11 was not heated after the deflagration had ceased.

Nos. 10, 12, 13, and 14 were heated to full redness for five minutes after deflagration had ceased.

It will be seen, from the results contained in the preceding table, that considerable uncertainty attends this method of proceeding;

* Nos. 5, 6, and 7 were portions of the same commercial sample of nitre, known to contain not less than 98 per cent.

† No. 8 consisted of a mixture of 95 parts of pure nitre with 3 parts of chloride of sodium and 2 parts of sulphate of potassa, made to imitate a specimen of commercial nitre. The quantity employed was 16·83 grains.

‡ Nos. 9, 16, and 17 consisted of a similar mixture, containing 90 per cent. of pure nitre.

for, although several of the numbers approach very nearly to those required by theory, others exhibit a very considerable deficiency, without any essential difference in the manner of conducting the experiments in each case.

Experiments were next made to determine whether the method of mixing the ingredients, or the degree and duration of the heat applied, exerted any important influence over the results. Some determinations, in which the materials were intimately mixed in a mortar and heated, in some cases merely with a spirit-lamp, in others to complete fusion of the mass, yielded results exhibiting similar discrepancies to those formerly observed.

After it had been shown, by experiments conducted in such a manner that the volatile products could be collected and examined, that no volatilisation of potassium took place during the deflagration, and that no appreciable amount of alkali remained adhering to the residual carbon, some determinations were made with a view of ascertaining whether the deoxidation of the nitre, in the presence of an excess of carbon, was in all cases complete.

60 grains of pure nitre, 15 of lamp-black, and 360 of chloride of sodium, were deflagrated at a fair red heat. The mass was extracted with water in the usual manner, and the residual charcoal weighed: it amounted to 6·1 grains. The aqueous solution was concentrated by evaporation, and mixed with strong sulphuric acid, when it evolved a powerful odour of chlorine, and exerted a decided bleaching action upon indigo, indicating the presence of nitric acid.

Another similar experiment, in which the usual quantities of the ingredients were employed, gave only 91·95 per cent. of nitre. The presence of unaltered nitric acid in the solution of the deflagrated mass was shown also in this case. A repetition of the experiment gave a similar result.

In two other determinations, the amount of alkali was estimated by the use of hydrochloric acid of known strength, in place of sulphuric acid; the neutralised solutions being subsequently evaporated, and the residues again ignited with an additional quantity of lamp-black, in order to determine quantitatively the nitre left unchanged.

1. 20 grains of nitre were employed; the amount of alkali produced in the first deflagration corresponded only to 19·34 grs., or 96·70 per cent. of nitre. The second deflagration of the neutralised residue gave 0·53 grs. of nitre, or 2·65 per cent.; giving a total of 99·35 per cent.

2. 20 grains of nitre yielded by the first deflagration 19·46 grs.,

or 97·3 per cent.; by the second, 0·59 of unaltered nitre: making in all 100·25 per cent.

Hence it will appear that, allowing for the unavoidable errors in these processes, the amount of nitre left unchanged after the first deflagration just supplied the deficiency.

Table IV. contains the results of some experiments made with the modifications above alluded to.

TABLE IV.

Exp.	Nitre found.	Nitre per cent.
1.	19·84	99·20
2*.	18·39	91·95
3†.	17·21	86·05
4†.	18·43	92·18
5‡.	19·64	98·20
6‡.	19·09	95·45
7.	19·59	97·95

In the preceding table, only those experiments are quoted which exhibited any remarkable deficiency. It must, in fairness, be stated that in some other experiments made under similar circumstances very satisfactory numbers were obtained, although no reason for the difference could be traced in the method of proceeding.

It naturally suggested itself that some alteration in the proportions of the ingredients might *ensure* a more accurate result; and with this view the experiments given in Table V. were undertaken.

TABLE V.

(Nitre employed, 20 grs.)

Exp.	Lamp-black.	Salt.	Nitre found.	Nitre per cent.
1§.	8·0	120	19·10	95·50
2.	10·0	120	20·10	100·50
3.	10·0	120	19·84	99·20
4‖.	3·0	120	18·59	92·95
5‖.	3·5	120	19·72	98·60
6.	3·5	120	19·59	97·95
7¶.	5·0	80	17·86	89·30
8**.	10·0	120	18·89	94·45

* No. 2 was heated in a muffle to complete fusion, after deflagration.

† Nos. 3 and 4 were made with an artificial mixture containing 95 per cent. of nitre.

‡ In Nos. 5 and 6 the residual carbon was weighed, and subsequently incinerated. In No. 5, 1·6 grs. of charcoal was left unconsumed, and yielded 0·11 of ash. In No. 6, 1·2 grs. of charcoal was left, and furnished 0·076 of ash.

§ In No. 1, 20·1 grs. of nitre were employed.

‖ In Nos. 4 and 5, nitric acid was detected after the deflagration, although some carbon was left unconsumed.

¶ No. 7 was made with a mixture containing 92 per cent. of nitre.

** No. 8 was projected by degrees into the crucible.

The numbers above quoted show that neither the increase nor the diminution of the amount of lamp-black was attended with any beneficial result. Indeed, the alterations in the proportions appeared to increase the chances of error, satisfactory results being much less frequently obtained.

On examining the various specimens of lamp-black employed in all the experiments alluded to, they were found to contain a very appreciable amount of sulphur. Since it was deemed possible that the presence of this impurity might exert some influence upon the results obtained, it was determined to substitute, for the lamp-black, charcoal obtained by the complete calcination of washed starch.

Table VI. contains results of some of the determinations made with this variety of charcoal.

TABLE VI.

(Nitre employed, 20 grs.)

Exp.	Charcoal.	Salt.	Nitre found.	Nitre per cent.
1.	10	80	21·60	108·00
2.	10	80	20·35	101·75
3.	10	80	21·10	105·50
4.	10	120	21·10	105·50
5.	10	80	21·05	105·25
6*.	10	80	20·60	103·00
7.	20	80	21·60	108·00
8.	20	80	21·35	106·75
9.	20	80	21·85	109·25
10.	30	80	20·22	101·10
11.	20	80	20·52	102·59 †

These results naturally excited surprise, as in every case the amount of carbonate of potassa indicated by the standard acid considerably exceeded that which corresponded to the amount of nitre present. They served, however, to recall to mind the circumstance that an excess had occasionally been obtained in the former experiments, in which lamp-black was employed, but on which little stress had been laid, since they were comparatively so seldom met with as to be attributed to some accidental circumstance.

* In No. 6 the quantities were doubled, 40 grs. of nitre being employed, to see whether the error was much diminished.

† Two experiments were made, in which wood-charcoal was substituted for charcoal from starch. The results were, in one case, 5·95 per cent., and in the second, 16·4 per cent., in excess.

Some of these results are collected in Table VII.

TABLE VII.

Exp.	Nitre found.	Nitre per cent.
1.	23·26	116·30
2*.	23·04	115·20
3†.	22·21	111·70
4‡.	22·40	112·00
5§.	19·09	95·45
6§.	19·14	95·70
7.	20·14	100·70
8.	20·05	100·25
9‖.	18·21	91·05

No other mode of accounting for the excess could at first be imagined, than to attribute it to the production of some soda from the chloride of sodium by the action of the carbon, and possibly a little moisture, at the high temperature produced by the deflagration; but a number of experiments, made under circumstances which were assimilated as nearly as possible to those of the deflagrations with nitre, showed that the slight amount of decomposition suffered by the chloride of sodium in a deflagration is quite insufficient practically to influence the results.

It next became necessary to examine the action of the standard acid upon the solution, coloured with litmus, in order to ascertain if any source of error could there be traced.

In some instances, when the solution had been neutralised before boiling, it was observed that the blue colour of the litmus returned when the liquid attained the boiling point, and that, even after repeated changes to red, by the addition of successive portions of acid the blue again made its appearance after boiling for some time.

1. A solution of chloride of sodium coloured with litmus was reddened with a drop of sulphuric acid, and boiled for a considerable time, but without effecting any change in its colour.

2. 10 grains of carbonate of soda dissolved in water, and coloured with litmus, required in the cold, in order to produce the peculiar brownish-red tint due to strong acids, 84·8 measures

* In No. 2, 20·3 grs. of nitre were employed.

† In No. 3, 19·36 grs. of nitre were employed; the determinations were conducted, at a moderate heat, over gas.

‡ No. 4 was heated very gently over a spirit-lamp.

§ Nos. 5 and 6 were mixtures containing 95 per cent. of nitre.

‖ No. 9 was a mixture containing 90 per cent. of nitre.

of the standard acid, corresponding to 9·58 grains of carbonate of soda. On boiling, the solution became perfectly blue. A second experiment gave the same result.

3. Several experiments were made in order to determine the difference between the amount of acid required to produce permanent redness in the cold, and subsequently, on boiling.

Table VIII. gives some of the results: —

TABLE VIII.

Exp.	Measures of acid employed. In the cold.	Upon boiling.
1.	65·80	68·20
2*.	74·20	87·00
3.	67·25	70·30
4.	69·50	72·50
5.	76·50	79·30
6.	62·00	64·80
7.	69·00	72·00
8.	70·00	73·50
9.	68·10	71·10
10.	75·20	78·00
11.	75·00	78·00
12.	71·00	73·20
13.	74·50	79·50
14*.	85·00	91·00
15*.	83·50	91·00
16*.	83·50	87·20
17*.	86·50	94·75

It will be seen that, in many of these determinations, the difference was scarcely greater than could be accounted for by the influence of the carbonic acid; and it was found that, in these cases, the amount of nitre indicated never exceeded the theoretical quantity; whereas, in those experiments which gave any considerable excess, a much greater amount of acid was required after the liquid was boiled.

An observation which had been made in several of the experiments seemed to throw some light upon this matter. It had been found that a very powerful ammoniacal odour was perceptible during the deflagration (even when all the materials had been carefully dried), and, on decomposing the alkaline solutions with

* These determinations were made with starch-charcoal.

sulphuric acid, a distinct odour of hydrocyanic acid was apparent, especially in cases where starch- or wood-charcoal had been used, and in which consequently an excessive result had been obtained.

The existence of cyanide of potassium in the fused mass was proved by qualitative experiments, and it appeared exceedingly probable that a certain quantity of cyanate of potassa was also formed, and by its subsequent decomposition furnished ammonia, whereby a larger quantity of sulphuric acid was neutralised than was actually required by the carbonate of potassa formed.

For the investigation of this question, a number of experiments were instituted with pure cyanide of potassium and cyanate of potassa.

9·545 grs. of pure cyanide of potassium, exposed for some time *in vacuo*, were dissolved in water; the solution was coloured with litmus, and very dilute sulphuric acid of known strength added, until the bright red colour was produced.* The amount of acid added corresponded to 9·31 grs. of cyanide of potassium. The solution was unchanged by boiling, and contained no ammonia.

9·64 grs. of cyanide of potassium were ignited for five minutes in a partially closed platinum crucible. Effervescence was observed in the fused mass. On dissolving in water, and adding the standard sulphuric acid to the solution coloured with litmus, the latter assumed the violet colour, when a quantity of the standard acid had been added, corresponding to 4·23 grs. of SO_3. To produce the bright red tinge, 4·48 grs. of SO_3 were required. On boiling the solution, it became decidedly blue, and required (in all) to produce permanent red colour, 6·84 grs. of SO_3. Abundance of sulphate of ammonia was detected in the boiled solution.

It will be observed that in this experiment a certain quantity of acid was required to convert the violet tinge into the bright red, which would indicate the formation of some carbonate of potassa, which was also indicated by the effervescence observed during the fusion of the cyanide. The very large quantity of the standard acid which was required to restore the red colour to the solution which had been rendered blue by boiling, denoted the presence of

* This experiment, as well as others made in a similar manner, showed that the hydrocyanic acid liberated produced no effect on the colour of litmus, the blue passing at once into bright red, without the intermediate violet stages seen in the case of carbonic acid. It was found, by direct experiment, that a solution of hydrocyanic acid added to blue litmus produced a similar effect to that of free carbonic acid, but that it had no effect upon the litmus when cyanide of potassium was present.

a considerable quantity of cyanate of potassa, which was confirmed by the subsequent detection of ammonia in the liquid.

10 grs. of pure carbonate of soda were mixed with 1·77 grs. of cyanide of potassium, and fused for five minutes in a partially closed crucible. To produce the violet tinge, 5·72 grs. of SO_3 were necessary; to convert this into the red, required 8·37 grs. of SO_3. The solution became perfectly blue when boiled, and required (in all) 8·95 grs. of SO_3 to produce a permanent red colour.

The bearing of this experiment upon the determination of nitre will be rendered evident if it be remembered that the quantity of that salt equivalent to the carbonate of soda and cyanide of potassium employed is 22·14 grs. The amount of nitre, calculated from the alkalinity determined *in the cold*, would have been only 21·15 grs., or 95·5 per cent.; while, calculated from the result obtained on boiling, it would have been 22·62 grs., or 102·1 per cent.

9·86 grs. of cyanide of potassium were mixed with 5 grs. of lamp-black, covered with a layer of that substance, and heated to redness for five minutes. The product required, in the cold, 4·87 of SO_3, to produce the violet tinge, 5·03 for the bright red, and 6·44 on boiling.

9·29 grs. of cyanide of potassium were heated, as before, with 5 grs. of lamp-black, but without any superficial layer. The product required, in the cold, 4·64 grs. of SO_3 for the production of the violet tinge, 4·8 for the bright red, and 6·34 on boiling.

In these experiments, the amount of cyanate produced is considerably diminished by the presence of the charcoal, and hardly any carbonate appears to be formed, the carbon being oxidised by the air in preference to the cyanate of potassa.

10·052 grs. of cyanide of potassium were mixed with 5 grs. of starch-charcoal, and heated as before. The mass fused completely in this instance. Its solution required, in the cold, to produce the violet tinge, 5·20 grs. SO_3; for the bright red, 5·62; and, on boiling, 7·01 to produce the permanent tinge.

9·403 grs. of cyanide of potassium were mixed with 20 grs. of starch-charcoal, and heated as usual. The mass only fused slightly at the bottom of the crucible. Its coloured solution was rendered violet, in the cold, by 4·7 grs. of SO_3; red, by 5·13 grs.; and required, on boiling, in all, 5·75 grs. SO_3.

These experiments render it sufficiently obvious that the presence of a considerable quantity of charcoal does not prevent the oxidation of the cyanide of potassium.

10·533 grs. of cyanide of potassium were mixed with 100 grs. of chloride of sodium and 20 grs. of starch-charcoal, and heated to redness for about five minutes. The mass had not fused, but merely agglutinated. Its aqueous solution, when coloured, required for the production of the violet tinge, 5·23 grs. of SO_3; for the bright red, in the cold, 5·75; and, upon boiling, for the permanent red colour, 7·08 grs. SO_3.

10·803 grs. of cyanide of potassium were mixed with 5 grs. of lamp-black and 120 grs. of chloride of sodium, and heated to redness for five minutes. The mass had fused. Its coloured solution became violet on addition of 5·55 grs. of SO_3; red, in the cold, with 5·83; and required, in all, for the production of the permanent red, upon boiling, 7·4 grs. SO_3.

In these cases, the conditions of the experiments were as nearly as possible the same as those under which the determinations of nitre were made. It will be seen that, under these circumstances, the production of cyanate was also very considerable.

It was expected that the oxidation of the cyanide of potassium, in cases where starch-charcoal was employed, would have been much greater, since, in the nitre determinations with starch-charcoal, a much larger excess was always obtained. In the case of the actual deflagration, however, the temperature was much higher where starch charcoal was used, on account of the very much smaller volume of that substance. Probably, under these circumstances, the conditions for the formation of cyanate would be more favourable.

Cyanate of potassa itself was next subjected to experiment.

20 grs. of cyanate of potassa were dissolved in cold water, the solution coloured with litmus, and treated with dilute sulphuric acid of known strength. The addition of the first few drops produced the peculiar wine-red colour. 3·28 grs. of SO_3 were added before the red shade was produced in the cold. On boiling the solution, it became quite blue; and this phenomenon was repeated after several successive additions of sulphuric acid, until 14·24 of SO_3, in all, had been added.

In a second experiment with the same quantity of cyanate of potassa, 3·28 grs. of SO_3 were required in the cold; 14 grs., in all, were finally required upon boiling the solution.

In both of these experiments the odour of cyanic acid was distinctly perceived upon the addition of sulphuric acid, showing that a considerable quantity of this acid escapes decomposition, although the excess of the sulphuric acid employed above that required to

neutralise the potassa shows that the presence of cyanate in the fused mass after deflagration would cause a considerable apparent excess of nitre to be obtained.

Although, in several instances where a considerable excess had been obtained, notable quantities of ammonia were detected in the neutralised solutions, concentrated by evaporation, it was deemed essential to obtain more direct evidence of the existence of cyanate of potassa in the products obtained by the deflagration of such a mixture as had on a former occasion furnished the greatest excess.

20 grs. of nitre, 20 of starch-charcoal, and 80 of salt were deflagrated in the usual manner. The agglutinated mass was finely pulverised, and digested twice for some minutes with strong alcohol. The insoluble portion was separated by filtration, washed with alcohol, and afterwards completely extracted with water. The alcoholic solution was evaporated, the residue dissolved in water, and the solution treated with sulphuric acid.* It became red, in the cold, upon the addition of 1 measure of acid; the blue colour, however, returned upon boiling, and 4·5 measures in addition were required. The aqueous solution was also treated as usual with the standard acid; it required 82·5 measures of acid in the cold, but became blue on boiling, and required 4·5 measures in addition. The quantity of nitre, inferred from the total amount of acid employed, was 20·73 grs., or 103·65 per cent.

Another experiment was made in the same manner; but in this case there was hardly any additional quantity of sulphuric acid required after boiling, indicating that, from some accidental circumstance, hardly any cyanate had been produced. In this instance, moreover, the quantity of nitre obtained corresponded as closely as could be expected with the theoretical quantity.

In a third experiment, the result closely resembled that obtained in the first.

In a fourth experiment, 21·38 grs. of nitre were obtained, or 106·9 per cent.

The cause of the excess having been satisfactorily ascertained to be the formation of cyanate of potassa, and the neutralisation of a portion of the sulphuric acid by the ammonia formed from the cyanate, some experiments were made with a view to obviate this cause of error, by an alteration in the conditions under which the deflagration was effected.

In some cases, the mixture was projected by degrees into a red-

* The acid used in these experiments contained 8·93 grs. of SO_3 in 100 measures.

hot crucible. In most of these, a considerable deficiency was obtained, owing to the carbon having been partly consumed without acting on the nitre. In only one instance, in which 5 grs. of wood-charcoal were employed, the result showed a considerable excess. No accurate results were obtained by the use of a protecting film of carbon during the deflagration, which confirmed the conclusions drawn from the direct experiments with cyanide of potassium.

The great object to be attained appeared to be the introduction of so powerful a reducing agency into the deflagrating mass, as should at the same time ensure the complete deoxidation of the nitre, and prevent the conversion of any cyanide of potassium into cyanate of potassa. A compound containing hydrogen and carbon appeared likely to fulfil these conditions, and recourse was at once had to resin, as being the substance best adapted for the purpose.

In carrying out this idea, considerable difficulties were experienced in adjusting the proportion of resin, and the degree of heat to be employed.

When 10 grs. of resin were employed for 20 of nitre (with 120 of salt), and the mass heated over an argand burner, a considerable quantity of cyanate of potassa was found in the solution, and yet only 14·94 grs. of nitre were indicated by the standard (hydrochloric) acid. The remainder of the nitre which had escaped deoxidation was determined by evaporating the solution, and igniting the residue with lamp-black. The deficiency was thus supplied. It would appear that, in this case, so much of the carbon and hydrogen were volatilised in an unoxidised state, that a sufficient quantity was not left to effect the deoxidation of the nitre.

When 20 of resin were employed, no cyanate was found in solution, but the quantity of nitre indicated was only 19·27 or 96·35 per cent.

It was supposed probable that a reduction of the proportion of chloride of sodium would have the same effect as increasing the quantity of resin, by concentrating its action upon the nitre. With this view, 80 grs. of chloride of sodium and 20 of resin were employed in the next experiment, but only 18·3 grs. of nitre, or 91·5 per cent., were obtained.

Since it appeared that, in this experiment, the moderate heat applied volatilised a great part of the resin before the temperature was sufficiently high to allow of deflagration, another experiment was made with 30 grs. of resin and 80 of chloride of sodium, and the crucible was at once heated to bright redness over the

Herapath blowpipe. But, in this case, only 16·15 grs. of nitre were obtained, or 80·75 per cent.

50 grs. of resin and 80 of salt were then employed, and the mixture heated over a gauze burner. A small quantity of cyanate was found in the solution, and the acid used indicated 20·24 grs. of nitre, or 101·2 per cent.

When 30 of resin and 100 of chloride of sodium were heated over a gauze burner, a considerable quantity of cyanate was found in the solution, and the alkalinity obtained corresponded to 21·53 grs. of nitre, or 107·65 per cent.

Another experiment, in which the proportion of salt was increased by 20 grs., gave exactly the same result.

The salt was now diminished to 80 grs., with the same proportion of resin, and the mass was heated to redness for one minute after all vapours had been evolved. A considerable quantity of cyanate was here found, and the result gave 20·78 of nitre, or 103·9 per cent.

A second experiment gave the same result.

Since so much cyanate of potassa was produced in these cases, it was deemed advisable not to prolong the application of heat after the deflagration had finished, and the experiments included in Table IX. exhibit the results which were obtained when the mixture was heated only as long as any vapour was disengaged.

TABLE IX.

(Nitre employed, 20 grs.)

Exp.	Resin.	Salt.	Nitre found.	Nitre per cent.
1.	20	120	19·74	98·70
2.	20	120	20·02	100·10
3.	25	120	20·02	100·10
4.	20	100	19·81	99·05
5.	30	80	19·99	99·95
6.	30	80	20·01	100·05
7.	30	80	19·98	99·90
8.	30	90	19·90	99·50
9*.	30	80	19·17	95·85
10*.	30	80	19·17	95·85
11*.	30	80	19·17	95·85
12.	30	80	19·84	99·20
13.	30	80	20·07	100·35

* In Nos. 9, 10, and 11, a mixture containing 95 of nitre, 3 of chloride of sodium, and 2 of sulphate of potassa, was employed.

An inspection of this Table will show that, although the results were generally pretty accurate, when 20 grs. of pure nitre were employed, there was still a tendency (especially where less than 20 grs. of nitre were taken, as in the impure samples) to the formation of cyanate, which was indicated by the action of the acid.

This observation suggested the expediency of trying a method whereby any chance of error resulting in the formation of cyanate might be obviated, by the addition, after deflagration, of a powerful oxidising agent, such as chlorate of potassa, whereby the conversion of the cyanate into carbonate might be effected. It appeared probable, at the same time, that the additional elevation of temperature, caused by the powerful action of the chlorate of potassa upon the unconsumed carbon, would exclude the possibility of nitre escaping conversion into carbonate.

In the first experiments in which chlorate of potassa was employed, the deflagration was conducted, according to the old method, with lamp-black, the chlorate being subsequently sprinkled over the mass, which was afterwards heated for two or three minutes to redness. The results of these experiments are exhibited in Table X.

TABLE X.

(Proportions employed: 20 of nitre, 5 of lamp-black, 80 of salt.)

Exp.	Nitre found.	Nitre per cent.
1.	19·82	99·08
2.	20·14	100·70
3.	20·02	100·10
4.	20·07	100·35
5.	19·96	99·80
6*.	18·94	94·70
7*.	18·94	94·70
8*.	19·05	95·25
9*.	18·94	94·70

The results obtained by this modification were very encouraging, and those furnished by the sample containing sulphate of potassa also showed that any chance of error arising from the formation of sulphide of potassium was also obviated by the use of chlorate of potassa.

In cases where much sulphate was present, it was found that

* These determinations were all made with a mixture containing 95 of nitre, 3 of chloride of sodium, and 2 of sulphate of potassa.

the deflagration caused by sprinking the chlorate upon the mass was so violent as to endanger the projection of a portion of the fused mass. In addition, the length of time required to filter off the unconsumed carbon and to wash out all the alkali, formed a serious objection to the process, when applied for commercial purposes. The finely-divided state of the carbon rendered it impossible to effect the accurate determination of the alkalinity without previous filtration.

The experiments made with resin having shown that much less carbon was left unconsumed than in the case of lamp-black, and that the small residual portion was in an exceedingly porous condition, and therefore readily oxidised, an endeavour was made to take advantage of this circumstance in order to avoid the necessity for filtering.

A series of trials eventually led to the adoption of the following process, as yielding the most trustworthy results.

20 grs. of the sample to be examined are intimately mixed, in the platinum crucible, with 30 grs. of finely-powered resin, and 80 grs. of pure dry salt. The crucible is then loosely covered, and a moderate heat applied with a gauze burner; the heat is maintained for two or three minutes after all evolution of vapour has ceased. The crucible is then allowed to cool to such an extent that the chlorate of potassa shall not fuse when sprinkled upon the mass. About 25 grs. of the chlorate are added so as to form a layer upon the surface. A very gentle heat is first applied, until most of the chlorate has been decomposed, when the temperature is raised to bright redness, and maintained in that state for two or three minutes. The mass should then appear completely liquid, and free from any floating particles of carbon.*

When cool, the mass is carefully shaken out of the crucible into a funnel, and the crucible and cover washed with boiling water. The mass is dissolved by a stream of hot water from a washing bottle, and the solution allowed to run into the flask in which the determination is to be made. The liquid is coloured with litmus, and neutralised as usual with standard acid.

Table XI. includes the results of experiments made in this manner with pure nitre.

* It was found that those determinations in which any carbon was left always gave a marked excess.

TABLE XI.

Exp.	Nitre found.	Nitre per cent.
1.	20·00	100·00
2.	20·00	100·00
3.	19·97	99·85
4.	19·97	99·85
5.	20·08	100·40
6.	20·08	100·40
7.	20·08	100·40

Although, in the three last experiments, the error is hardly greater than would be permitted in such a process, it is obvious that accurate results would be obtained with greater certainty if the acid were graduated by determining the mean quantity required by 20 grs. of pure nitre, when deflagrated with the above precautions.

Some of the determinations, included in Table XII. of the amount of pure nitre contained in certain artificial mixtures, were calculated from the amount of standard acid employed in Nos. 5, 6, and 7 of Table XI.

TABLE XII.

Exp.	Nitre found.	Nitre per cent.
1*.	19·01	95·05
2†.	17·81	95·45
3‡.	17·90	89·50
4.	17·86	89·30
5.	18·01	90·05
6.	17·97	89·85
7.	17·97	89·85
8.	18·01	90·05
9.	17·99	89·95

Although the recent experiments made with this method have been most satisfactory, it could have been desired that more numbers might have been added to the above list. The accuracy of such a process can only be fully confirmed by extensive

* Nos. 1 and 2 were made with a mixture consisting of 95 of nitre, 3 of salt, and 2 of sulphate of potassa.

† In No. 2, only 18·655 grs. of the impure nitre were employed.

‡ Nos. 3 to 9 were made with a mixture consisting of 90 of nitre, 5 of salt, and 5 of sulphate of potassa.

practical application; and the authors hope, on a future occasion, to submit to the Society the results of such a trial.

It may not be out of place to direct attention to the most interesting of the general conclusions which have been arrived at, in the course of the above experiments.

1. That a considerable quantity of nitre may escape decomposition at a high temperature, even when intimately mixed with an excess of finely-divided carbon, and although vivid deflagration of another portion of the nitre had taken place in its immediate neighbourhood.

2. That, in the deflagration of a mixture of nitre, salt and charcoal, binoxide of nitrogen is evolved in large quantity; an observation which has also been incidentally made in the case of far more energetic deflagrations.

3. That a considerable quantity of cyanide of potassium is formed in these deflagrations, and that, even where much care had been taken to remove moisture from the materials employed in the experiments, a notable quantity of ammonia was evolved. An attempt, suggested by this circumstance, was made to determine nitre by ignition with charcoal and soda-lime, when the greater part of its nitrogen was obtained in the form of ammonia.

4. That the oxidation of cyanide of potassium by exposure to air at a high temperature is not prevented by the presence of carbon in a finely-divided state, or even by covering it with a layer of carbon.

The relations of nitre to different forms of carbon at a high temperature appear to present so many points of interest, whether viewed in relation to theory or to practice, that the authors have resolved to devote their earliest leisure to the investigation of the subject.

VI.—*Note on a New Method of Making Ferricyanide of Potassium and a Paracyanogen Compound.*

By LYON PLAYFAIR, C.B., F.R.S.

THIS note refers to two processes which only deserve description because they are of an unusual kind, and may possibly be employed for other purposes.

I.—*Ferricyanide of Potassium.*—When yellow prusside of potassium is precipitated by salts of lime or baryta, well-known sparingly soluble precipitates are obtained, containing 2 equivalents of barium or of calcium, instead of 2 equivalents of potassium. If R represent either of these metals, the formula of the precipitate is Fe_2Cy_6, K_2R_2. When these precipitates are treated with carbonate of ammonia, the earthy carbonates fall, and a solution is obtained of a salt $Fe_2Cy_6, 2K, 2NH_4$.

When this latter yellow salt containing ammonia is boiled with peroxide of manganese finely divided, ferricyanide of potassium is abundantly formed; and after the ebullition has been continued for some time, a portion of the solution filtered will be found to give no further precipitate with perchloride of iron, being wholly converted into a ferricyanide. During the boiling with the peroxide of manganese, ammonia is freely given off. The salt formed by this process in solution has all the properties of a ferricyanide, and would obviously be Fe_2Cy_6, K_2NH_4, in which 1 equivalent of ammonium replaces 1 equiv. of potassium in the red prusside. But this salt, by prolonged boiling with peroxide of manganese, is further decomposed, a green-coloured precipitate occurring, while the salt in solution still retains the ordinary characters of a ferricyanide, but contains less ammonium, more potassium, and generally an excess of iron. A salt of silver made from the red solution, and possessing the ordinary characters of the ferricyanide of silver, gave on analysis 10·89 per cent. of iron, and 60·28 per cent. of silver: calculation gives 10·44 per cent. of iron, and 60·45 per cent. of silver. This analysis leaves no doubt as to the character of the variable red salt in solution, though it contains, like the latter, an excess of iron.

The formation of the ferricyanide is clearly owing to an oxidation of the ammonium.

$$Fe_2Cy_6 2K, 2NH_4 + 2MnO_2 =$$
$$Fe_2Cy_6 2K, NH_4 + NH_3 + HO + Mn_2O_3.$$

It is well known that when ferricyanide of potassium is boiled with ammonia, a ferrocyanide is produced, 1 equiv. of hydrogen replacing 1 equiv. of potassium in the ordinary yellow salt. The presence of an excess of peroxide of manganese in the reaction now described appears to prevent this decomposition, as ammonia is given off during the whole oxidation.

I do not describe this formation of ferricyanide as an economical process for procuring the salt, but as an instance of an unusual process of oxidation which may be applied to other purposes.*

II.—*Paracyanogen Compound.*—In making the nitroprussides, I had found that, when cyanogen was in the nascent state, it combined with 2 equivalents of water, and produced oxamide:

$$Cy + 2HO = 2CO, NH_2.$$

Either this substance or paracyanogen might, therefore, be expected from hydrocyanic acid if the hydrogen were subjected to oxidation. For this purpose, 1 equiv. of ferricyanide of potassium was mixed with an equivalent of potash; and to this mixture was added an equivalent of hydrocyanic acid, the purpose being to liberate the cyanogen under favourable circumstances. The reaction expected was as follows:—

$$Fe_2Cy_6, 3K + KO + HCy = Fe_2Cy_6 4K + HO + Cy.$$

On adding the hydrocyanic acid to the mixture of red prusside and potash, the solution becomes yellow in colour, but soon passes to a dark red, or even black colour,—a bulky precipitate of a similar colour falling down. During this action, a small quantity of gas is observed to escape. The formation of the precipitate is much favoured by the solutions being warm: when they are dilute, it is even necessary to raise them nearly to the boiling point.

The bulky reddish-black precipitate is collected on a filter, and washed with cold water, in which it is scarcely soluble. It dissolves readily in water containing caustic soda or potash, and may

* Ferricyanide of potassium may also be procured under the following circumstance, which deserves inquiry, as the reaction must be somewhat complicated. Common prusside of copper has the formula $Fe_2Cy_6 3CuK$. When this salt is treated with caustic ammonia in the cold, a very pale red-coloured solution is obtained, which, boiled with peroxide of manganese, gives ordinary ferricyanide of potassium. Analysis gave the following results:—

I. 12·26 grains gave 3·00 peroxide of iron, and 9·605 sulphate of potash.
II. 14·225 grains gave 3·49 peroxide of iron, and 11·19 sulphate of potash.

	I.	II.	Calculated.
Iron . . .	17·12	17·17	17·02
Potassium . .	35·11	35·26	35·56

be purified in this way from a small quantity of oxide of iron which may fall down with it: it is again precipitated from the alkaline solution by the addition of an acid.

The precipitate contracts much in bulk during drying. It loses about $10\frac{1}{2}$ per cent. of water at 212°. Specimens obtained at different times did not give constant results.

	First Preparation.		Second Preparation.		Third Preparation.
	I.	II.	I.	II.	
Carbon .	40·050	40·240	42·053	42·415	38·918
Nitrogen .	41·618	—	42·772	—	—
Hydrogen	3·400	3·393	3·324	3·318	3·252
Oxygen .	14·932	—	11·851	—	—
	100·000		100·000		

From these analyses it is obvious that the compound is not simply paracyanogen. Not only is the carbon in too large proportion to the nitrogen, but the hydrogen is more than sufficient to convert the oxygen into water. In the preparation of the substance, a little gas is always observed to escape,—due, probably, to the oxidation of a portion of the paracyanogen. The substance as prepared is therefore impure, and requires proper inquiry.*

Not being able, without interfering with another investigation, to pursue the subject further, in the very limited time which I have at my disposal for scientific pursuits, Baron Liebig has kindly placed it in the hands of one of his pupils for investigation.

* I find that the same substance can be procured by passing chlorine through cyanide of potassium. Purified by solution in soda, precipitation by hydrochloric acid, and washing, two preparations dried at 212° gave the following results on analysis :—

	First Preparation.		Second Preparation.
Carbon . .	36·22	35·200	35·200
Nitrogen. .	—	42·300	—
Hydrogen .	3·150	3·000	3·030
Oxygen . .	—	19·500	—
		100·000	

In this case, the carbon and nitrogen are nearly in the proportion to form cyanogen, but the hydrogen is in excess to the oxygen on the supposition that it was present as water. It should be mentioned that, on treating this black compound with nitric acid, a yellow substance is obtained, which, as I have only made one analysis, I do not venture to describe.

VII. — *On the Sulphovinates; and on Amylophosphoric Acid and the Amylophosphates.*

By FREDERICK GUTHRIE, B.A., Ph.D.
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WITH respect to the rational constitution of the sulphovinates, chemists are at present so far agreed as to admit in them the presence of sulphuric acid. An objection was formerly raised to this view, on the ground that the sulphuric acid could not be shown to exist, as such, by means of the usual reagents; and it was assumed that the salts in question contained hyposulphuric acid. This position has, however, been overthrown, partly by the discovery of isethionic acid, partly by the observed behaviour of other compounds of ethyl, such as the chloride and sulphide of ethyl, in which the chlorine and sulphur are much more difficult to recognise by means of nitrate of silver than is the case with the soluble inorganic compounds of these bodies.

A question, however, which still has to be answered, is — "In what *manner* do the sulphovinates contain the sulphuric acid?"

Those chemists who look upon sulphuric acid as a bibasic acid, and express the composition of its hydrate by the formula $2HO,S_2O_6$, view, for the most part, the salts of sulphovinic acid as basic sulphates, one of whose atoms of base is potash, and the other oxide of ethyl. They accordingly class sulphovinate of potash with the so-called double salts of sulphuric acid, such as the potassio-sulphate of zinc.

$$\left.\begin{matrix} ZnO \\ KO \end{matrix}\right\} \cdot S_2O_6, \text{ Sulphate of potash and zinc.}$$

$$\left.\begin{matrix} C_4H_5O \\ KO \end{matrix}\right\} \cdot S_2O_6, \text{ Sulphate of potash and ethyl.}$$

Now, in the first place, this view is contradicted by the fact that the oxide of ethyl in the second of these salts cannot be driven out by a more powerful base, as is the case with its analogue, the oxide of zinc, in the inorganic sulphate. Even on continued boiling with potash, the ether is not given off as alcohol. The difficulty of maintaining this view, again, is materially increased when we reflect that in the neutral sulphate of ether, $\left.\begin{matrix} C_4H_5O \\ C_4H_5O \end{matrix}\right\} \cdot S_2O_6$, the one atom of ether may be eliminated or exchanged for water

or a base much more easily than the other, and that the so-called neutral ethers, such as acetic, nitric, or oxalic ether, on being boiled with caustic potash, are transformed, under formation of alcohol, into the potash salts of the corresponding acids.

These considerations render it more than doubtful whether the metallic oxide and the oxide of ethyl be equally basic in function. It seemed desirable that new facts should be gained for the elucidation of this point. I imagined that such facts might be furnished by the behaviour of an aqueous solution of a sulphovinate towards the galvanic current. For if, in the sulphovinate of potash, both the potash and ether be united as base with the sulphuric acid, we should be justified in expecting, on electrolysing a concentrated aqueous solution of this salt, that, at the + pole, sulphuric acid and oxygen would be liberated, and, at the − pole, potassium, (potash and hydrogen), together with ethyl, (or ether or some ethyl compound, possibly hydride of ethyl).

Into a cold, concentrated, aqueous solution of sulphovinate of potash, free from sulphate of potash, I accordingly introduced two platinum electrodes in such manner that they were separated by a porous clay cell. The electric current from four of Bunsen's carbo-zinc elements was sufficient to effect a lively disengagement of gas at both poles, accompanied by an evolution of heat which rendered cooling from the exterior necessary. In a short time the liquid surrounding the + pole showed a strong acid reaction. The gas which was here liberated smelt distinctly of aldehyde, and consisted of oxygen and carbonic acid. The liquid at this pole gave, with chloride of barium, a white precipitate which was insoluble in hydrochloric acid. Sulphuric acid was therefore present in the free state. At the same time, the liquid at the − pole assumed an alkaline reaction, and the gas there liberated proved to be pure hydrogen. I satisfied myself, by careful examination, of the entire absence of all carboniferous gases, nor could I detect at this pole the slightest traces of ether or alcohol.

It was imagined that the sulphuric acid and the aldehyde, which appeared at the + pole, might be secondary products of decomposition, effected by the oxygen, *in statu nascenti*. To get rid of this secondary decomposition, I formed the + pole of amalgamated zinc. On completing the circuit, a lively disengagement of gas took place at the − pole, as before, while, on the other hand, at the + pole, no gas at all was liberated, and neither aldehyde nor sulphuric acid were formed. The zinc electrode, however, soon became covered with a pellicle of sulphovinate of zinc, which, after

a time, broke the electric current. Again, a fresh solution being taken, the liquid at the + pole was made strongly alkaline with carbonate of potash. On the introduction of platinum electrodes, carbonic acid was plentifully liberated at the + pole, but as no sulphate of potash could be detected, it followed that this was due to the liberation not of sulphuric, but of sulphovinic acid.

In the same manner, making use of platinum electrodes, I electrolysed an aqueous solution of amylo-sulphate of potash, and recognised precisely analogous phenomena. At the + pole, oxygen was liberated and a distinct smell of valerianic acid noticeable. The solution around this pole became acid, and contained sulphuric acid. At the — pole, the liquid became distinctly alkaline, and the gas there liberated was, as before, pure hydrogen. The slightest traces of fusel oil or amylic ether would at once have been recognised by their powerful odour, had they been separated. The liquid at the — pole remained inodorous.

From these experiments I believe the conclusion may legitimately be drawn, that, in amylosulphate and sulphovinate of potash, the oxides of ethyl and amyl have not the same function as the potash, but that they are combined with the sulphuric acid in a different, and, as it appears, a more intimate manner. The fact that, on electrolysis, these organic oxides remain with the sulphuric acid, and accompany it to the + pole, shows that the potash alone is the electropositive constituent of these salts, and that the formula $\left.\begin{matrix}KO\\C_4H_5O\end{matrix}\right\}\cdot S_2O_6$ expresses a hypothesis on the constitution of sulphovinate of potash which rests upon false assumption.

It seemed to me of importance to examine in a similar manner the ethylophosphates, and to see whether in these the organic oxide is liberated at the + pole, as in the sulphovinates, or whether it goes to the — pole. For this purpose, the amylophosphate of potash was chosen, because, if the oxide or hydrated oxide of amyl were liberated, together with the metallic oxide, at the — pole, it would be at once recognised by the mere odour. On introducing the platinum electrodes into a concentrated aqueous solution of amylophosphate of potash, separated into two portions by a clay cell, hydrogen was liberated at the — pole, and oxygen, together with carbonic acid, at the + pole. The solution at the latter pole assumed an acid reaction, and smelt distinctly of valerianic or butyric acids (evidently secondary products of decomposition). The liquid at the — pole became alkaline, but remained odourless.

From this it would appear that in the amylophosphates, and, generally, in the ethylophosphates, we are not at liberty to assume that the organic oxides are combined in the same manner as the metallic oxides; that is, as base. Accordingly, we must not understand the ordinary formulæ for ethylo- and amylophosphate of potash,

$$\left.\begin{matrix}2KO\\C_4H_5O\end{matrix}\right\}\cdot PO_5,\ \text{and}\ \left.\begin{matrix}2KO\\C_{10}H_{11}O\end{matrix}\right\}\cdot PO_5,$$

as if the organic oxides played the same part in them as does the basic water in the ordinary tribasic phosphate of potash, $\left.\begin{matrix}2KO\\HO\end{matrix}\right\}\cdot PO_5$; but we must rather assume that the phosphoric acid, together with the oxide of amyl, forms a bibasic amylophosphoric acid.

As amylophosphoric acid and its salts have only lately become known, I subjoin a description of their preparation and properties.

AMYLOPHOSPHORIC ACID.

If about equal weights of hydrated phosphoric acid and hydrated oxide of amyl be shaken in a bolt-head till perfect mixture occurs, the two unite with considerable elevation of temperature, and the mixture assumes a pale red tinge. The mixture is allowed to remain for about twenty-four hours in a place of about 60°—80° C. temperature. The liquid assumes a fine wine-red colour during this time, and the formation of amylophosphoric acid takes place. It is now to be repeatedly shaken with warm water, which removes the amylophosphoric acid, together with the free phosphoric acid, from the uncombined fusel-oil. The wash-waters are collected, slightly supersaturated with carbonate of potash, and evaporated on a water-bath almost to dryness. The mass obtained in this manner consists of amylophosphate of potash, together with phosphate and traces of carbonate of potash. To get rid of the last two, the mass is digested with warm spirits of wine and quickly filtered. The phosphate and carbonate of potash remain for the most part on the filter, while the amylophosphate of potash is in the filtrate. The filtrate is now evaporated almost to dryness upon a water-bath. This process has to be frequently repeated, stronger spirits being employed each time, and at last absolute alcohol, the last filtration being performed with the exclusion of air. The separation is only complete when a portion of the almost dry mass, dissolved in water, gives a snow-white precipitate with nitrate of silver.

The substance obtained as above is a yellowish, gelatinous,

transparent body, still containing combined alcohol. To get rid of this alcohol, it is sufficient to dissolve the mass repeatedly in water, and to evaporate to dryness on a water-bath. A honey-coloured mass is thus obtained, consisting of minute crystals of pure amylophosphate of potash.

This salt is a tenacious, finely crystallised, translucent body, without odour, but having the well-known peculiar taste of the other compounds of amyl. On exposure to the air, it absorbs moisture, and deliquesces to a syrupy transparent liquid of feeble smell. If it be dried, as far as possible, on a water-bath, and then heated in a tube by itself, or with hydrate of potash, it yields fusel-oil. Heated on platinum foil in the flame of a lamp, it burns with a pure white flame, leaving pyrophosphate of potash as residue. This decomposition is accompanied by a striking inflation of the mass, due probably to the escape of mechanically and chemically combined water. Amylophosphate of potash is soluble in every proportion in hot and cold water; it is soluble also in alcohol, but insoluble in ether. On account of the difficulty of freeing it completely from water, I have not subjected it to analysis. From the composition, however, of the salts formed from it, its composition doubtless corresponds with the formula $\left.\begin{matrix}2KO \\ C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5$.

As most of the amylophosphates are insoluble, or difficultly soluble, they may be readily prepared from the potash-salt by double decomposition. They are, in general, somewhat more soluble than the corresponding salts of tribasic phosphoric acid, and because the latter is unquestionably the more powerful acid; it may be completely removed by fractional precipitation, if its presence in the amylophosphate be suspected. Those salts which are insoluble in water are, like the phosphates, easily soluble in dilute nitric and hydrochloric acids. The amylophosphates are, generally speaking, more stable than the sulphovinates and ethylophosphates, inasmuch as they bear boiling with water without decomposition.

Amylophosphate of Lead, $\left.\begin{matrix}2PbO \\ C_{10}H_{11}O\end{matrix}\right\} PO_5$, is precipitated from a dilute solution of amylophosphate of potash on the addition of acetate of lead. The precipitate, carefully washed and dried at 100° C., is a bulky white powder, without taste or smell; it is easily soluble in hydrochloric and acetic acid. It contains no water. On analysis it gave the following result:—

a. 0·6335 grm. of the salt, dried at 100° C., was treated with

fuming nitric acid, in order to effect decomposition; the mass was then dissolved in water, and the lead precipitated by hydrosulphuric acid. The phosphoric acid in the filtrate was precipitated as ammonio-phosphate of magnesia. The lead determination was lost. The weight of the pyrophosphate of magnesia was 0·2034 grm., corresponding to 0·1290 grm. phosphoric acid.

b. 0·6772 grm. dried at 100° C. was ignited in a porcelain crucible, treated with fuming nitric acid, and warmed, then boiled with water, and the lead precipitated by sulphuric acid. Alcohol being added, the whole was filtered, the filtrate boiled, and the phosphoric acid estimated as pyrophosphate of magnesia. The above quantity yielded 0·5507 grm. sulphate of lead, or 0·3764 grm. lead; and 0·2163 grm. pyrophosphate of magnesia, or 0·1373 grm. phosphoric acid.

c. 0·4834 grm. dried at 100° C. was burned with oxide of copper, pieces of previously fused chlorate of potash being introduced at the end of the tube, and copper turnings being placed in the anterior. On account of the small relative quantity of organic matter present, it is advisable to employ five or six decigrammes. The above quantity gave 0·2474 grm. carbonic acid, or 0·0749 grm. carbon; and 0·1419 grm. water, or 0·0157 grm. hydrogen.

The composition *per cent.*, as found and calculated, is accordingly—

	Calculated.	Found.		
		a.	*b.*	*c.*
$2Pb$	= 55·39	—	56·4	—
C_{10}	= 16·02	—	—	15·5
H_{11}	= 2·93	—	—	3·2
PO_5	= 19·23	20·4	20·2	—
O_3	= 6·43	—	—	—
	100·00			

Amylophosphate of Silver, $\left.\begin{matrix}2AgO\\C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5$, is precipitated from a solution of amylophosphate of potash, on the addition of nitrate of silver, as a white bulky precipitate. The pure white colour of this combination is, as mentioned before, a good means for testing the purity of the potash-salt. Exposed to the light, this silver salt becomes grey; it remains white in the dark. It is appreciably soluble in warm water, but does not separate in the crystalline form on cooling. On long continued boiling with water it is decomposed, silver being deposited. Heated on a platinum foil it be-

comes yellow, leaving for residue pyrophosphate of silver. The salt employed for analysis was dried at 100° C.

a. 0·6404 grm. was ignited in a porcelain crucible with previously fused nitrate of potash. The mass thus obtained was drenched and digested with dilute nitric acid. From the clear solution thus obtained the silver was precipitated with hydrochloric acid, and the phosphoric acid with sulphate of magnesia and ammonia. In this manner 0·4782 grm. chloride of silver (=0·3599 grm. silver), and 0·1842 grm. pyrophosphate of magnesia (=0·1169 grm. phosphoric acid) were obtained.

b. 0·5631 grm. treated as above yielded 0·4198 grm. chloride of silver (=0·3159 grm. silver), and 0·1612 grm. pyrophosphate of magnesia (=0·1023 grm. phosphoric acid).

c. 0·4072 grm., burnt with oxide of copper with the same precautions as with the lead salt, gave 0·2300 grm. carbonic acid and 0·1197 water (=0·0627 grm. carbon and 0·0133 hydrogen).

d. 0·4204 grm. gave 0·2340 grm. carbonic acid and 0·1260 water (=0·0638 grm. carbon and 0·0140 grm. hydrogen).

Hence the following composition *per cent.*:—

	Calculated.	Found.			
		a.	*b.*	*c.*	*d.*
$2Ag$	= 56·39	56·19	56·10	—	—
C_{10}	= 15·66	—	—	15·39	15·18
H_{11}	= 2·87	—	—	3·26	3·33
PO_5	= 18·78	18·26	18·16	—	—
O_3	= 6·20	—	—	—	—
	100·00				

Amylophosphate of Copper, $\left.\begin{matrix}2CuO \\ C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5$, is precipitated from a dilute solution of amylophosphate of potash on the addition of a dilute solution of sulphate of copper. The precipitate is at first almost perfectly white; it assumes after a time a bluish tinge, and in the dry state is a light blue amorphous powder. This copper salt may be heated to 110° C. without decomposition ensuing.

a. 0·7633 grm. was ignited, the mass obtained dissolved in hydrochloric acid, and the copper precipitated by hydrosulphuric acid. The washed sulphide was dried, and mechanically separated as perfectly as possible from the filter. The filter was burned, and its ash, together with the sulphide of copper, was treated with fuming nitric acid. After dilution, the sulphur was separated by filtration, and the copper precipitated by potash. The filtrate from

the sulphide of copper was boiled to expel the hydrosulphuric acid, and the phosphoric acid precipitated as ammonio-phosphate of magnesia. The above quantity gave 0·2691 grm. oxide of copper (=0·2149 grm. copper), and 0·3658 grm. pyrophosphate of magnesia (0·2323 grm. phosphoric acid).

b. 0·4366 grm. gave 0·4108 grm. carbonic acid (=0·1120 grm. carbon), and 0·1882 grm. water (=0·0209 grm. hydrogen).

	Calculated.	Found.	
		a.	*b.*
$2Cu$	= 27·70	28·1	—
C_{10}	= 25·98	—	25·6
H_{11}	= 4·76	—	4·8
PO_5	= 31·16	30·4	—
O_3	= 10·39	—	—
	100·00		

Amylophosphate of Baryta, $\left.\begin{matrix}2BaO \\ C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5$, is precipitated from a solution of amylophosphate of potash, on the addition of chloride of barium, in the form of white scales of a silky lustre. This salt is slowly precipitated from cold solutions; its formation, and especially the formation of the scales, is favoured by gentle heat. Although the specific gravity of the baryta-salt is doubtless greater than that of the copper compound, yet the former collects principally at the surface of the liquid,—a phenomenon which may possibly be ascribed to the fatty nature of the body.

For the determination of the baryta and the phosphoric acid, weighed portions of the substance were ignited, the residues digested with dilute nitric acid, and the liquid containing the baryta and phosphoric acid filtered from the carbon. The baryta was then precipitated by sulphuric acid, and the phosphoric acid as ammonio-phosphate of magnesia.

a. 0·4588 grm. gave 0·3473 grm. sulphate of baryta (=0·2043 grm. barium), and 0·1692 grm. pyrophosphate of magnesia (=0·1074 grm. phosphoric acid).

b. 0·5730 grm. gave 0·4358 grm. sulphate of baryta (=0·2565 grm. barium), and 0·2122 grm. pyrophosphate of magnesia (=0·1347 grm. phosphoric acid).

c. 0·4013 grm., burned as above with oxide of copper, gave 0·2796 grm. carbonic acid and 0·1531 grm. water (=0·0763 grm. carbon and 0·0170 grm. hydrogen).

Hence the following composition *per cent.*:—

	Calculated.	Found.		
		a.	*b.*	*c.*
$2Ba$	= 45·07	44·54	44·76	—
C_{10}	= 18·73	—	—	19·00
H_{11}	= 3·62	—	—	4·24
PO_5	= 23·68	23·4	23·5	—
O_3	= 7·89	—	—	—
	99·99			

In a solution of subnitrate of mercury, amylophosphate of potash produces a precipitate in the form of a white amorphous powder, the composition of which has not been determined.

Amylophosphate of Ammonia, $\left.\begin{matrix}2H_4NO\\C_{10}H_{11}O\end{matrix}\right\}PO_5$. For the preparation of this salt, freshly precipitated amylophosphate of copper may be suspended in water and treated with freshly prepared sulphide of ammonium. The filtrate from the sulphide of copper is then boiled, again filtered, and evaporated to dryness on a water-bath. It is, however, in this process impossible to avoid the formation of sulphite and sulphate of ammonia. These impurities may be removed by recrystallisation from alcohol. In its external properties, the ammonia compound prepared as above has great similarity to the potash salt. The same body is obtained in a state of greater purity by the direct neutralisation of amylophosphoric acid by ammonia.

Amylophosphoric Acid.—For the preparation of free amylophosphoric acid, I made use of the freshly-prepared and well-washed copper salt. This salt was suspended in water, and the copper precipitated from it by a stream of hydrosulphuric acid. The liquid, filtered as quickly as possible from the sulphide of copper, reacted strongly acid; it was evaporated to the consistence of a syrup on a water-bath. A drop of this syrupy mass, dissolved in water and neutralised by ammonia, gave a pure white precipitate with nitrate of silver,—a proof that the acid had neither been decomposed by the precipitation of the copper nor by the evaporation on the water-bath. At this stage of concentration, the acid did not lose weight over sulphuric acid. After replacement on the water-bath, minute crystals were formed, which, under the microscope, proved to be long needles.

Amylophosphoric acid, prepared as above, is without odour, has

a strong acid taste, and easily expels carbonic acid from combination. It is soluble in water and alcohol, but insoluble in ether, so that it is precipitated on mixing a concentrated alcoholic solution with ether. The crystallised acid eagerly absorbs moisture from the air, and deliquesces: I was in consequence unable to procure a quantity of the dry acid sufficient for analysis. From the composition of its salts, however, we are justified in supposing its formula to be—

$$\left.\begin{matrix}2HO\\C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5.$$

Amylophosphoric acid is distinguishable from ethylo- and amylosulphuric acids, as well as from ethylophosphoric acid, by its greater stability; inasmuch as the former three acids, even in dilute solution, are quickly decomposed on the application of heat, while the latter, in concentrated solution, bears the heat of a water-bath without undergoing decomposition. Heated in the flame of a lamp, it burns with a white flame, leaving a residue of phosphoric acid.

If dry amylophosphate of silver be introduced into a tube, moistened with a few drops of chloride of amyl, and the tube be then hermetically sealed and exposed for several hours to a temperature of about 180° C., decomposition ensues. On the one hand, chloride of silver is found; and on the other, an ethereal liquid, which is taken up by alcohol, and reprecipitable therefrom in oily drops on the addition of water. The smell of this body is distinctly different from that of fusel-oil, as well as from that of chloride of amyl. It is probably amylophosphate of oxide of amyl, the formation of which may have occurred according to the equation:

$$\left.\begin{matrix}2AgO\\C_{10}H_{11}O\end{matrix}\right\} \cdot PO_5 + 2(C_{10}H_{11}Cl) = 3C_{10}H_{11}O \cdot PO_5 + 2AgCl.$$

Unfortunately, I had not sufficient of this body for analysis.

VIII.—*On the Action of Heat upon the Oxychloride of Copper (Atacamite.)*

By FREDERICK FIELD.

SOME time since a paper was published by me in the "Memoirs of the Chemical Society," "On the Composition of a Specimen of Atacamite from the province of Copiapo, Chili." As I have fre-

quently met with this mineral since in various parts of Atacama, and at different times have had large quantities to smelt, and opportunities of observing its behaviour under the influence of heat, I thought perhaps a few remarks would not be uninteresting, more especially as the results obtained by me upon this native oxychloride of copper differ considerably from those of Proust and others upon the artificially prepared compound.

In Gmelin's "Handbook of Chemistry," (Cavendish Society,) Vol. v. p. 440, under the head of "Mono-hydrated Oxychloride of Copper," it is said, upon the authority of Proust, that a compound having the composition $CuCl, 3CuO$ is obtained by gently heating the hydrated compound $CuCl, 2CuO + HO$, and that at a red heat oxygen is given off, and it is converted into a compound of protoxide and dichloride of copper, $CuCl, 3CuO = Cu_2Cl, 2CuO + O$. It is also called by Proust, p. 438, same volume, "Cupric oxide with cuprous chloride, the residue obtained by heating cupric oxychloride." In p. 441, same volume, the hydrated cupric oxychloride found in nature as atacamite when heated, according to the experiments of A. Vogel, gives off hydrochloric acid.* In the same page, the composition is given as under, viz.:—

Chloride of copper . . .	30·17
3 Oxide of copper . . .	53·72
4 Water	16·11
	100·00

The mass of mineral upon which I experimented had, as nearly as possible, the same composition:—

Chloride of copper . . .	30·94
Oxide of copper	53·31
Water	16·12
	100·00

or $CuCl, 3CuO + HO$, which requires 15·87 per cent. chlorine, 16·11 per cent. water, and 57·29 per cent. oxide of copper. On placing 100 grs. of the above mineral finely powdered in a platinum crucible, and exposing it with every precaution for half an hour to a heat gradually increasing to whiteness, it was found on reweighing to have lost 46·32 grs. and appeared a deep black powder without any shade of brown or other colour. It will be seen from

* Vogel's observation appears rather to refer to the artificially prepared compound.

this that the loss on heating exactly corresponds with the sum of the water and chloride of copper the mineral originally contained, viz., 47·06 per cent. The residue should then consist of nothing but pure black oxide. It was dissolved in pure nitric acid, and tested for chlorine by nitrate of silver. A merely perceptible cloud of chloride of silver was obtained, which is accounted for by a trace of the sublimed chloride of copper remaining on the upper part of the crucible. The silver was separated by HCl, and the copper estimated in the usual way.

53·31 grs. gave 42·61 copper = 79·94 per cent.,
calculation being 80·00.

During the whole time of heating, a dense white smoke was developed, which condensed as a yellow powder when any cold surface was introduced. A glass rod, dipped in solution of ferrocyanide of potassium and held over the fumes, became instantly covered with the rose-coloured ferrocyanide of copper. I could not in these experiments collect sufficient of the sublimate for analysis. I had to operate upon a larger quantity. Two or three hundred-weight of specimens containing comparatively small portions of the oxychlorides (from 4 to 5 per cent.) were heated with a quantity of charcoal and wood shavings in a small furnace somewhat resembling a lime-kiln loosely covered. When the ore had become thoroughly red hot, white fumes arose, and condensed on the cover and the superior layer of mineral, as a brilliant yellow sublimate, highly crystalline in appearance. These were removed with great care, placed at once into a weighed stoppered glass bottle, and subjected to the heat of an air-bath. It was perfectly impossible to handle them or to expose them one moment to the colder air, as they turned at first snow-white, and then green, owing to absorbed water.

25 grains of this yellow sublimate were dissolved in water, and yielded upon analysis 13·13 chlorine and 12·86 copper=52·52 per cent. of the former and 47·46 of the latter, or as nearly as possible pure anhydrous chloride of copper.

From the above experiments it appears that the chloride, when associated with the oxide of copper, comports itself in a different manner than when in its uncombined state, in the latter case being converted into dichloride with loss of chlorine; but even this compound is itself dissipated at a white heat. I am led to believe that in the decomposition of the oxychloride there is no intermediate stage in the process, such as the conversion of the protochloride

into the dichloride, but a direct disengagement of the former from its associated oxide, in the first place, because the characteristic flame is uniform throughout from the moment of heating, and in the second, because the evolved sublimate consists of pure anhydrous chloride of copper.

The following formula might be offered for oxychloride of copper, although I confess no experiments of mine have been able to prove that such is the fact.

$$Cu_2\overset{Cl}{O},2CuO+4HO$$

We have here 2 equivs. of copper combined with 1 equiv. oxygen and 1 equiv. chlorine, and coupled with 2 equivs. of protoxide, so that 1 equiv. of chlorine might be supposed to have replaced 1 equiv. of oxygen in 4 equivs. of the oxide of copper,

$$4CuO+Cl-O=Cu_2\overset{Cl}{O},2CuO$$

and upon the application of heat, either two equivalents are acquired, or the atom may be supposed to be divided.

$$2(Cu_2\overset{Cl}{O},2CuO+4HO)=2CuCl+6CuO+8HP$$

When the oxychloride is heated with lime, chloride of calcium is formed, together with black oxide of copper.

IX.—*Analysis of a Meteoric Stone from the Desert of Atacama.*

By Frederick Field.

The following is an analysis of a meteoric stone which fell sometime since in Bolivia, about a hundred leagues from the coast North of the port of Cobiza. A portion sent me by a friend had a stony metallic appearance, was very hard and tough, of specific gravity 7·89. In various cavities upon the surface were minute crystals of a brownish white colour, which on analysis were found to contain silica, lime, oxide of iron, and phosphoric acid. A

portion broken off from the metallic part, and analysed, gave nickel, iron, phosphorus, and traces of cobalt; no vestige of sulphur could be detected. The following is the quantitative analysis—

Iron . . .	87·80
Nickel . . .	11·88
Phosphorus .	00·30
	99·98

with traces of cobalt.

The phosphorus was estimated as phosphate of magnesia. The sulphides of nickel and iron, dissolved in dilute aqua-regia, were separated by succinate of ammonia. The stone was perfectly soluble in dilute hydrochloric acid.

X.—*Some Experiments illustrative of the Reciprocal Decomposition of Salts.*

By J. H. Gladstone, Ph.D., F.R.S.

Among the conclusions arrived at by me in a paper published in the "Philosophical Transactions" of last year, were the following:—

"Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions."

"These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture."

My impression is that these laws are of universal application; but this can be established only by the observation of a large number of varied instances in which they hold good, and by the investigation and explanation of every supposed exception.

The present paper contains the account of some reactions bearing upon the subject, which are of value, either from the experiments having been performed with elements hitherto untried, or from some novelty in the mode of observation. Every difficulty which,

to my knowledge, has been proposed by others, or which has occurred to my own mind, has been examined, and is here commented on.

Chromium Salts.—The soluble chromic salts have very remarkable optical properties. Their colour, by transmitted light, depends not only for its depth, but for its very character, upon the amount of salt which the ray has traversed in the solution. If the solution be weak, or if only a thin stratum be seen, it appears green; if a stronger solution or a thicker stratum, it appears red. As these two colours are complementary, or nearly so, the red on dilution passes into the green, not by a strictly speaking intermediate shade, but by a kind of brown or neutral tint. Now though, as far as I am aware, this description applies to all the soluble chromic salts, the amount of oxide requisite to give the red appearance depends greatly upon the acid with which it is combined. Thus, if equal portions of chromic oxide be dissolved in acetic and in sulphuric acids, it is very easy to arrange it so that, when viewed through glasses of equal capacity, the acetate appears red, and the sulphate green. If now to the red acetate a few drops of sulphuric acid be added, it passes through the neutral tint to the green colour; or if contrariwise, a little glacial acetic acid be added to the green sulphate, it assumes the reddish hue.

It is interesting to observe this change of colour by means of a prism. If a luminous object be viewed through any solution of a chromic salt, it exhibits two images, the one red, and the other green, fringed with blue. The relative intensity of colour of these two images differs with the amount of salt looked through, and with the character of the electro-negative element. On the addition of acetic acid, the red image becomes comparatively brighter and brighter, while the green image pales; and contrariwise, on the addition of hydrochloric or sulphuric acid, the green image becomes comparatively more and more distinct, while the red one fades. Again, if a solution of the acetate be seen through the sides of a wedge-shaped glass vessel, the stratum near the angle will appear green, that near the broad end red, while about a certain line neither colour will preponderate. On the addition of sulphuric acid this line advances towards the broad end, while acetic acid brings it again nearer the angle.

Ferrous Salts.—The mutual displacement of sulphuric and acetic acids may be also rendered visible by means of the protoxide of iron. If to a green solution of sulphate of iron a solution of acetate of potash be added, a brown colour is the result. If sulphuric acid

be added to this, the pale colour is more or less restored; if an addition of acetate of potash be then made, the brown reappears. This may be repeated many times with the same solution.*

Cobalt Salts.—The sulphocyanide of cobalt in an anhydrous condition, like the chloride, is blue; but, unlike that salt, it retains its blue colour when dissolved in a little water. As the solution is diluted, it gradually assumes the red tint which characterises solutions of the compounds of this metal. If very strong solutions, containing corresponding equivalents of chloride of cobalt and sulphocyanide of potassium, be mixed, a blue colour makes its appearance, showing the formation of sulphocyanide of cobalt. But that the double decomposition has not been complete, may be made evident by carefully diluting the blue mixture with water till it has become distinctly red, and dividing it into two parts. If to the one portion some of the very strong solution of sulphocyanide of potassium be added, the blue colour is restored; on the addition of more water, it disappears; and this may be repeated a number of times, until ten or twelve equivalents of sulphocyanide of potassium has been added to one of chloride of cobalt. If, inversely, to the other portion of the original mixture chloride of cobalt be added, that substance also produces a blue colour, which may be likewise caused to become red, or to reappear many times, by the successive addition of water or chloride of cobalt.

Chromates.—During the past year the "Journal de Pharmacie et Chimie"† has published an extract, in which Margueritte proves that "chromic acid can displace hydrochloric, nitric, and even sulphuric acids, and take away from them a part of the base to which they are united, whether that base be strong or weak." We all know that these acids are capable of displacing chromic acid; indeed, the same investigator has shown that even boracic and carbonic acids will decompose bichromate of potash. By a method of observation almost identical with that adopted by myself, he found that the addition of such salts as chloride of potassium, or the nitrate or sulphate of potash or ammonia, to a solution of the red bichromate of potash, caused the production of yellow monochromate. Such experiments, he conceives, lend support to his view of "the partition of a base between the two acids, when any acid is added to any saline solution;" which is identical with the

* This experiment was suggested by a remark in Professor Miller's Chapter on "Some Circumstances which Modify the Operations of Chemical Affinity," in his "Elements of Chemistry, Theoretical and Practical," vol. ii.

† J. Pharm. [3] xxvii. 21.

law of Berthollet, or rather is included in the more general expression.

One objection, however, may be taken to this conclusion from Margueritte's experiments. It may be contended that the salt added merely displaces the one equivalent of chromic acid in the bichromate of potash, and that, in fact, the reaction is according to the formula:

$$KO,2CrO_3 + KO,SO_3 = 2(KO,CrO_3) + SO_3.$$

Indeed, this idea seems to have been in the mind of Schweizer, in a paper published a few months ago on these reactions of chromic acid.* The point seemed to admit of easy determination, for if the decomposition really take place in that manner, the production of the yellow colour will be perfect when single equivalents of the two salts are mixed, and no subsequent addition of sulphate of potash will lighten the tint. On trying the experiment it was found to be otherwise. The addition of one equivalent of sulphate of potash to one of bichromate of potash caused certainly a diminution of the red tint; but successive additions of the sulphate to the previous mixture caused the yellow to become more and more decided. Hence it may be concluded, that the mixture of single equivalents contains both bichromate and monochromate of potash, besides sulphuric acid and sulphate of potash, and possibly free chromic acid.

Copper Salts.—M. Alvaro Reynoso has recently published some "facts relating to the double decomposition of salts."† By taking advantage of the power of glucose to reduce the acetate of copper, he finds that when acetates of the alkalies, earths, or metals, are mixed with the nitrate or sulphate of copper, the acetate of that metal is produced. This is, so far, in accordance with the law of Berthollet; but whether the decomposition be complete or not does not appear from his experiments, though the action of mass is very evident in some of them. One remark, however, presents some difficulty. He observed that acetate of copper, mixed with ferric nitrate or sulphate, loses the property of being reduced by glucose. This I have repeated quantitatively. Solutions of acetate of copper and nitrate of iron were prepared of known strength; they were mixed together in certain proportions, with the addition of glucose, and boiled.

* J. pr. Chem. lxv. 173. † Compt. rend. xli. 278.

Salts mixed with glucose.	Result.
Acetate of copper	Immediate decomposition.
3 eq. „ „ + 1 eq. ferric nitrate	Deposit after boiling.
3 eq. „ „ + 1·5 eq. „ „	Deposit after long boiling.
3 eq. „ „ + 2 eq. „ „	Deposit after very long boiling.

From this it may be concluded that $3(CuO,AcO_3)+Fe_2O_3,3NO_5$ do not become wholly $3(CuO,NO_5)+Fe_2O_3,3AcO_3$. This also was confirmed by the colour: for the mixture of two equivalents of the ferric nitrate with three of acetate of copper was deeper in tint than when the salts were mixed in the proportions merely necessary for the above double decomposition.

This reaction, then, instead of militating against the conclusion illustrated in this paper, serves to support it.

In the "Comptes rendus" for last year, there also appear papers by Tissier* and Bineau,† narrating experiments confirmatory of the views arrived at by myself and other investigators; but they call for no further remark.

EVIDENCE FROM CIRCULAR POLARISATION.

Camphorates.—It was an early idea of mine that the effect of chemical affinity among substances in solution might be tested by means of circular polarisation; yet the evident intricacies of the subject deterred me from making any experiments: nor, indeed, did I see a case suited to my purposes. M. Bouchardat,‡ however, has announced that camphoric acid dissolved in alcohol causes a right-handed rotation; and that when it is saturated with a base, the rotation is considerably diminished, but is restored again on the supersaturation of the base by another acid. Yet, if I understand his experiments rightly, it appears that in the latter case the original amount of rotation is not quite obtained. Thus he gives the numbers:—

Camphoric acid	12° R.
The same, saturated with soda	7° R.
The same, supersaturated with hydrochloric acid	11° R.
Camphoric acid	22° R.
The same, saturated with ammonia . . .	12° R.
The same, supersaturated with hydrochloric acid	21° R.

* "On some Facts relating to Double Decomposition," p. 362.

† "On the Solubility of certain Metallic Oxides and Earthy Carbonates, and on some Reactions produced by their Solutions," p. 509.

‡ Compt. rend. xxviii. 319.

Are we wrong in deducing from these results that the hydrochloric acid did not completely decompose the alkaline camphorates first formed?

SALTS DISSOLVED IN ACIDS.

Sulphate of Baryta.—Within these last few months, no less than four papers have appeared, in which the solubility of sulphate of baryta in hydrochloric acid is discussed. Professor Rose,* Mr. Crace Calvert,† Dr. Noad,‡ and Messrs. Nicholson and D. Price,§ have shown by independent experiments, not only that sulphate of baryta is, to a certain extent, soluble in these acids, but that the amount dissolved is most materially diminished by the presence of an excess of baryta salt. Rose states that the solution of pure sulphate of baryta in either of the above-mentioned acids gives a small precipitate when treated with either chloride of barium or dilute sulphuric acid. He says, "It is a striking circumstance that the presence of the dissolved sulphate of baryta is indicated by both these reagents," and he concludes that the salt in question "is less soluble in sulphuric acid and in chloride of barium than in hydrochloric acid and nitric acid." Yet the great analytical chemist can scarcely offer this as a satisfactory explanation; for, in the experiment, the acid solvent still remains, capable, of course, of exerting its former power. Indeed, the next sentence shows the insufficiency of the reason; for Rose remarks that sulphate of baryta does not separate from the acid solution by means of water, although it is assuredly less soluble in water than in hydrochloric or nitric acids.

However, this "striking circumstance" is precisely what might be expected if the law of reciprocal decomposition, as quoted above, be true. If sulphate of baryta in excess be treated with an acid—say nitric—that portion which is brought into solution will suffer partial decomposition, and a solution will eventually result, containing as much sulphate of baryta as the free acid is capable of dissolving, and as much nitrate of baryta and sulphuric acid as is capable of counterbalancing the two other bodies. Such being the case, the addition of either sulphuric acid or baryta salt will disturb the equilibrium, with the production of fresh sulphate of baryta, which must precipitate, seeing that the acid solution was previously saturated.

Sulphate of Strontia.—Rose observed the same with sulphate of

* Pogg. Ann. xcv. 108.
† Proc. Roy. Soc. vii. 532.
‡ Chem. Soc. Qu. J. ix. 15.
§ Phil. Mag. 1856 [4], xi. 169.

strontia as he did with sulphate of baryta. Of course it is capable of the same explanation.

Sulphate of Lime.—On examining a solution of sulphate of lime in hydrochloric acid, Rose observed that a precipitate formed when it was treated with sulphuric acid, but not when it was treated with a solution of chloride of calcium. That this precipitation by sulphuric acid is incapable of the explanation offered by him in the case of sulphate of baryta, he shows by the observation that "a concentrated solution of sulphate of lime in water is *not* precipitated by sulphuric acid." But the non-precipitation by chloride of calcium presented a difficulty to my explanation.

Two possible reasons suggested themselves to me, and, fortunately, each was capable of being put to the test of experiment. It might be that one equivalent of sulphate of lime is capable of being dissolved (or decomposed) by not more than one equivalent of hydrochloric acid. In that case, the formation of any amount of sulphate of lime from chloride of calcium would set free an equivalent amount of hydrochloric acid, which would keep it in solution. It was found, however, that one equivalent of sulphate of lime required three equivalents of hydrochloric acid (somewhat dilute) at the ordinary temperature to dissolve it.

The other supposition was that chloride of calcium might itself exert a solvent action on sulphate of lime; but this was found not to be the case.

The only supposition, then, that seemed possible, if my view were correct, was that such a small amount of additional sulphate of lime was formed that it was soluble in the water which was added at the same time as the chloride of calcium. This, happily, was also capable of being put to the proof by employing a very concentrated solution of the chloride. On doing so, a cloudiness at once appeared, which soon became a decided precipitate of crystallised sulphate of lime.

These reactions are all explicable on the supposition that when sulphate of lime is dissolved in hydrochloric acid, nearly (but not quite) all is converted into chloride of calcium.

Though sulphate of lime is not rendered more soluble in water by the presence of chloride of calcium, it does dissolve more freely when *other* chlorides are present. A. Vogel* has shown this in reference to chloride of ammonium and common salt: I have tried the experiment with four metallic chlorides—those of zinc, copper, iron, and chromium, and have found it to be the case with each.

* J. pr. Chem. xi. 196.

Now this is precisely what might be expected, supposing the two salts to suffer reciprocal decomposition, with the conversion of more or less of the sulphate of lime into the very soluble chloride. Vogel observes that when the solution in chloride of ammonium is evaporated to dryness, and heated to redness, pure sulphate of lime remains; and this has been employed as an argument against Berthollet's views: yet when we reflect how very volatile is the ammoniacal chloride, while the sulphate is not volatilised without decomposition, we shall see that no other final result could be obtained.

Sulphate of Lead.—Wackenroder* states that sulphate of lead dissolved in nitric acid is precipitable by sulphuric acid. I find that such a solution gives a precipitate also when treated with nitrate of lead.

This case is mentioned, because a statement of Wackenroder has been employed as an argument against the Berthollian hypothesis. The German chemist says that sulphuric acid, in large quantity, precipitates the sulphate of lead *completely*, notwithstanding the presence of the nitric acid. Yet, farther on in his paper, he proves that the said precipitation is *not* absolutely complete, and it is evident that, by employing the word "*vollständig*," he merely meant to say that the action was sufficiently perfect for ordinary analytical purposes.

Sulphate of Mercury.—Wackenroder also shows that the insoluble sulphate of mercury dissolved in nitric acid is precipitable by sulphuric acid.

Oxalate of Lime.—In order to vary these observations by experiments on other salts than sulphates, a saturated solution of oxalate of lime in dilute hydrochloric acid was prepared. On the addition of oxalic acid, a white precipitate after a while made its appearance; and on the addition of chloride of calcium to another portion, a precisely similar result ensued.

Chloride of Lead.—Dilute nitric acid was saturated with chloride of lead, and divided into two portions. To the one, hydrochloric acid was added, which caused an instantaneous precipitate; to the other, nitrate of lead was added, and, after some time, long crystals of chloride of lead formed.

Phosphate of Iron.—Hitherto the fact, that when a salt insoluble, or slightly soluble, in water, has been dissolved in an aqueous solution of any acid, the base divides itself in certain proportions between the two acids, has been deduced merely from the reactions

* Ann. Ch. Pharm. xli. 316.

of which such a solution is capable. It seemed desirable to prove this, if possible, by direct ocular demonstration. Phosphate of iron appeared to offer an opportunity of doing so. It is white in the solid state, but dissolves in hydrochloric acid with an orange colour. Now, if this colour be due to ferric chloride, we have a means of judging whether the whole of the iron be in that condition. Accordingly, some dilute hydrochloric acid was saturated with ferric phosphate. A portion was found to contain the same amount of colour as an aqueous solution of 0·067 grm. of ferric chloride; but the acid liquid itself consisted of 0·585 grm. of ferric phosphate dissolved in 0·477 grm. of real hydrochloric acid. Evidently, therefore, the whole of the iron was not in the state of chloride; indeed, supposing the ferric phosphate to have been of the usual composition, $2(Fe_2O_3)3PO_5$, the amounts of iron in the two equi-tinted solutions were—

In the solution containing both phosphoric and hydrochloric acids . . .	0·164 grm. Fe.
In the solution of pure ferric chloride .	0·023 „ „

Hence it would appear, that when ferric phosphate is dissolved in the smallest possible amount of hydrochloric acid, only one-seventh part is converted into the chloride.

It is here assumed that the ferric phosphate, which is white in its pure state, has no colour of its own when dissolved. In other ways, also, the above numbers may not be very exact; yet one thing is certainly proved,—that when phosphate of iron is dissolved in a minimum of hydrochloric acid, it is not wholly, or principally, converted into the chloride.

It may be expected that if a considerable amount of the iron still remain as phosphate, the addition of more hydrochloric acid will decompose more or less of this, and increase the colour. Such was found to be actually the case.

These experiments could not be advantageously performed by looking horizontally through the solution, for the golden tint of the ferric chloride is very little altered by dilution. A comparison, however, is easily made by looking perpendicularly through the solutions contained in glasses of uniform diameter.

The addition of phosphoric acid to the acid solution of ferric phosphate gave an immediate flocculent precipitate. I failed, however, to obtain a precipitate on the addition of ferric chloride. This is the first exception to the general inference that if a salt AB dissolve in an acid CD, the addition of either AD or CB will cause the production of more AB than the acid can keep in solu-

tion; yet when the peculiarity attending the saturating power of phosphoric acid is considered, it will probably present no great difficulty to the reception of that as a general law.

REPUTED EXCEPTIONS.

Beside the *primâ facie* difficulties already discussed, other reactions have been urged against the general conclusions adopted by me, and these claim a careful examination.

Cyanide of Mercury.—Reactions of an apparently anomalous character take place among mercury salts: thus, the cyanide affords two instances where an insoluble compound does not form, although, from the reciprocal decomposition of the compounds mixed together, it might be expected to make its appearance. When the cyanide of mercury is treated with potash in solution, the insoluble oxide does not precipitate; and when mixed with nitrate of silver it produces none of the insoluble cyanide of that metal.

The first of these apparent anomalies depends perhaps on the formation of the well-known oxycyanide of mercury, which is a ternary compound soluble in water. The annexed formula represents this decomposition:—

$$2HgCy + KO = Hg_2CyO + KCy$$

though such a mixture may contain, I apprehend, simultaneously all the four substances, besides the double cyanide of mercury and potassium.

As to the second anomaly, cyanide of mercury forms a soluble crystalline double salt with nitrate of silver, which has been analysed by Wöhler,* who assigns to it the compositition $AgO, NO_5, 2HgCy, 4HO$. But were we to overlook this, the decomposition might be supposed to take place thus:—

$$3(HgCy) + 3(AgO, NO_5) = HgCy, HgO, NO_5 + 2Ag\,Cy, AgO, NO_5 + HgO, NO_5$$

all of which, beside the original salts, are soluble in water.

Boracic Acid.—The objections most frequently urged are founded on the behaviour of boracic acid. It is contended that this acid has no power to decompose sulphate of potash, and that borax is completely decomposed by an equivalent of sulphuric acid. I have already shown† that the non-alteration in colour of litmus does not prove this, but I have in vain sought for some property which would enable us to decide what actually does take place in the above-mentioned mixtures. Indications, however, have been ob-

* Pogg. Ann. i. 231.

† Phil. Trans. 1855, 220.

tained where boracic acid was mixed with another sulphate, and also where it was mixed with another potash salt; and in each of these cases it was found capable of effecting some decomposition.

The borate of quinine in solution, like the hydrochlorate, is non-fluorescent, or nearly so. If boracic acid be added to a neutral, and consequently non-fluorescent solution of sulphate of quinine, it immediately exhibits the beautiful surface blue, just as though a drop of hydrochloric acid had been added, and doubtless from the same cause—the formation of some bisulphate through the abstraction of some of the quinine by the other acid.* The addition of a very large quantity of boracic acid appeared to diminish the colour, and consequently to indicate the decomposition of the bisulphate; but I certainly never succeeded in destroying the fluorescence, as is easily done when the powerful hydracids are employed.

Three solutions were prepared—the first of boracic acid, the second of pure nitrate of potash, the third of a mixture of the two; and they were digested for some time with metallic copper, after which the solutions were tested with ammonia in excess. The first showed absolutely no blue, the second only a faint trace, while in the third the blue colour was very decided. From this it may be inferred that the boracic acid had displaced some of the nitric acid, which in its turn had attacked the copper. The quantity of copper dissolved must, however, have been exceedingly small.

It has also been objected that boracic acid occasions no precipitate in a solution of nitrate of lime, although borate of lime is an insoluble salt. Now there are said to be compounds of boracic acid and lime, which are not insoluble in water: and, moreover, the production of borate of lime from the nitrate must liberate an equivalent amount of nitric acid, which of course will exert its own solvent power. But while the non-precipitation of a borate is evidently inconclusive as to what really happens in the mixture, it appeared to me that metallic copper would also in this case furnish an indication. The experiment was accordingly tried as with the potash salt, and it was found that the neutral nitrate of lime had no action on copper, while the mixture of nitrate of lime and boracic acid produced a solution which was rendered blue by ammonia, and during the digestion a gelatinous substance formed in small quantity about the shreds of copper.

* See Stokes's paper, Phil. Trans. 1852, 542; also, 1855, 210.

It thus appears that boracic acid is able to displace other acids from their combinations, though but to a slight extent, in the cases just examined.

REGULAR PROGRESSIVE CHARACTER OF THE INFLUENCE OF MASS.

From the experiments detailed in the paper already referred to, I was led to the conclusion, that—"An alteration in the mass of any of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regular progressive ratio; sudden transitions only occurring where a substance is present, which is capable of combining with another in more than one proportion." Yet there is one experiment recorded which appears to offer an exception, and to indicate changes of ratio somewhat similar to those observed by Bunsen and by Debus, in cases where the resulting compounds were not capable of reacting. This experiment is where a solution of oxalate of lime in hydrochloric acid was precipitated by the addition of acetate of potash or soda. The table drawn out, and the curves projected from the experiments, show considerable irregularities; but as each experiment consists of six or eight separate observations, it was thought desirable to repeat the experiment, taking every precaution to ensure the observations being all made under the same circumstances.

Into each of ten glasses were poured 400 grain measures of a solution of oxalate of lime in hydrochloric acid. Different amounts of a solution of acetate of potash were mixed thoroughly with these, and the solutions were made up to the same bulk by the addition of water. After standing twenty-four hours, the resulting precipitates were washed the same number of times by suffusion and decantation; they were then boiled with pure water, and collected.

Oxalate of lime in hydrochloric acid.	Acetate of potash added.	Oxalate of lime precipitated.
400 gr. meas.	50 gr. meas.	0·015 grm.
400 „	100 „	0·049 „
400 „	150 „	0·102 „
400 „	200 „	0·136 „
400 „	250 „	0·193 „
400 „	300 „	0·278 „
400 „	350 „	0·336 „
400 „	400 „	0·350 „
400 „	500 „	0·354 „
400 „	600 „	0·354 „

On the addition of potash to the filtrate from the last experiment of this series, a slight turbidity was produced, from the separation of oxalate of lime, showing that the whole of the hydrochloric acid had not even in that case been converted into chloride of potassium.

From the table it will be seen that a larger addition of acetate of potash caused a larger deposit of oxalate of lime, and that in a ratio which, though somewhat remarkable, was tolerably regular in its character. As it may be interesting to know the proportionate equivalents of the substances in each experiment, they are given in the annexed table. The initial 400 grain measures of acid solution contained 0·375 grm. of oxalate of lime, dissolved in 2·26 grms. of hydrochloric acid, nearly the proportion of 1 equiv. to 12; and each 100 grain measures of the acetate of potash solution contained 1·80 grm. of the anhydrous salt.

Oxalate of lime.	Hydrochloric acid.	Acetate of potash.	Oxalate of lime deposited.
1 equiv.	12 equiv.	1·75 equiv.	0·04 equiv.
1 „	12 „	3·5 „	0·12 „
1 „	12 „	5·25 „	0·27 „
1 „	12 „	7· „	0·36 „
1 „	12 „	8·75 „	0·51 „
1 „	12 „	10·5 „	0·74 „
1 „	12 „	12·25 „	0·90 „
1 „	12 „	14· „	0·93 „
1 „	12 „	17·5 „	0·95 „
1 „	12 „	21· „	0·95 „

The examination of these new substances, and of those reactions which appeared to be exceptional, tends therefore only to confirm the former conclusions. I propose to investigate, as they arise, any further objections founded on experiment.

REPORT OF THE COUNCIL

OF THE

CHEMICAL SOCIETY,

MARCH 31, 1856.

THE Council are glad to be able to congratulate the Society again upon its steady prosperity, as will appear from the following statement of the number of Fellows, and of the Accounts as reported by the Treasurer.

The total number of Fellows is . . .	256
Deaths and resignations since the last Anniversary Meeting	6
Fellows admitted since last Anniversary . .	9
Increase	3

Fellows deceased:—

Professor J. F. W. Johnston, M.A., F.R.S., Durham.
Professor J. E. Bowman, King's College, London.
Mr. W. Richardson, Denmark-hill.

James F. W. Johnston was born at Paisley in the year 1796. Part of his early childhood was spent in Manchester, whither his father for a time removed, but afterwards settled with his family at Kilmarnock. Young Johnston was at early age thrown upon his own resources, and, during the time that he was studying in the University of Glasgow, supported himself for some years by private tuition. In 1825, he took the charge of a proprietary school in Durham, and in the year 1830, married one of the daughters of Mr. Ridley, of Park End. Being now possessed of a competence which enabled him to follow his scientific tastes, he

shortly afterwards proceeded to Stockholm, with the view of studying chemistry in the laboratory of Berzelius.

In the year 1833, the University of Durham was opened, and the Readership of Chemistry and Mineralogy was conferred upon Mr. Johnston. He continued to hold this office during the remainder of his life; but for many years, excepting during term time, he resided in the neighbourhood of Edinburgh.

In 1843, he was appointed chemist to the Agricultural Society of Scotland. When that Society was dissolved, he left Edinburgh, and took up his abode at Durham, and it was here that he expired, on the 15th September, 1855, in the 59th year of his age.

Professor Johnston published several memoirs upon different purely chemical subjects. Amongst the best known of these, is his paper upon Paracyanogen; one upon the Vanadiate of Lead; on a particular Hydrate of Sulphate of Lime; and besides these he published several other Mineralogical and Geological papers. The "Philosophical Transactions" for 1839-40, contain an elaborate series of researches by Professor Johnston on the resins. He also communicated to this Society, in 1842, a short paper upon the peculiar sugar contained in the manna of the Eucalyptus, which has since been more fully studied by Berthelot.

Professor Johnston took a warm interest in the earlier proceedings of the British Association, and contributed some valuable reports to its Transactions, particularly one upon the present state of chemistry, which appeared in the volume for the year 1832.

But it was as a clear expositor of Science that he was particularly distinguished. His most attractive work, and the one best known to the general reader, is that on the "Chemistry of Common Life," which exhibits his peculiar facility of imparting scientific truth, often of an abstruse kind, in a form acceptable to the non-scientific reader. It displays the extensive reading of the author, and the discriminative skill which characterized him, in no ordinary degree, in the choice and arrangement of his materials.

The most important works published by Professor Johnston are those which relate to Agricultural Chemistry. His lectures on Agricultural Chemistry and Geology contain a fund of sound and carefully digested information upon the subjects to which they relate, and the work constitutes the most complete systematic treatise upon those subjects, that has yet appeared. This work has passed through several editions; but one of his smaller works upon the same subject, the "Catechism" of Agricultural Chemistry, has attained a degree of popularity, which, for a scientific work, is

probably unexampled; it has passed through thirty-three editions in this country, independent of numerous large editions in America, and it has been translated into various European languages.

Professor Johnston travelled widely both upon the Continent of Europe, and in America. He has left an agreeable account of part of his transatlantic experience, in his "Notes on North America." And he had just returned from an extensive journey in Central Europe, which he had undertaken, in connection with some geological inquiries in which he was engaged, when he was seized with a pulmonary attack, which terminated his life in a few days after his arrival at his own residence at Durham. Professor Johnston was one of the original members of the Chemical Society.

Mr. John Eddowes Bowman was also one of the original members of this Society. After a period of study in the laboratory of the late Professor Daniell, of King's College, he settled for a while at Manchester, where he availed himself of the facilities afforded him for becoming familiar with many important branches of manufacturing chemistry.

In the year 1845, he removed to London on the occasion of his appointment as Demonstrator of Chemistry in King's College, and on the creation of the Chair of Practical Chemistry in that Institution in 1851, he was selected as its first occupant. In the year 1846, Mr. Bowman contributed to the Transactions of the Society a paper on Tribasic Boracic Ether, but the feeble state of his health during the latter years of his life precluded him from active exertion in the laboratory. He is well known, however, as the author of two useful manuals, one on Practical Chemistry, the other on Medical Chemistry; each of which has gone through two or three editions. Mr. Bowman possessed the art of interesting his pupils strongly in the subject which they were studying, and from the clearness and facility with which he imparted information was highly popular with his class.

During the last three years of his life, Mr. Bowman withdrew almost entirely from general society. The strength and excellence of his character was, therefore, comparatively little known; but the few who shared his intimacy feel that with him they have been parted from a Christian friend, whose loss will not be easily replaced. Early in the month of February of the present year, he was attacked with influenza, which speedily reduced his already

enfeebled frame, and he expired on the 10th of February, in the 36th year of his age.

The following is a List of the Papers read before the Chemical Society between March 30, 1855, and March 31, 1856 :—

"On the Composition of the Waters of the Metropolis during the Autumn of 1854:" by Dr. R. D. Thomson.

"On Platinised Charcoal:" by Dr. J. Stenhouse.

"On the Preparation of Strontium and Magnesium:" by Dr. Matthiessen.

"On the Preparation of Lithium:" by Professor Bunsen.

"On the Colour of Chloride of Copper in different States of Hydration:" by Dr. J. H. Gladstone.

"On the Proximate Constitution of Chemical Compounds:" by J. J. Griffin.

"A Few Notes on Barium:" by Dr. Matthiessen.

"On the Hydro-Electrical Currents Generated by Couples Formed of Single Metals:" by Richard Adie.

"On the Volatile Oil of *Ptychotis Ajowan*:" by R. Haines.

"On the Action of Light upon Chloride of Silver:" by F. Guthrie.

"On Azobenzole and Benzidine:" by Alfred Noble.

"On Insolinic Acid:" by Dr. A. W. Hofmann.

"Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre:" by F. A. Abel and C. L. Bloxam.

"On the Solubility of Sulphate of Baryta in Hydrochloric Acid:" by Dr. Noad.

"On a New Class of Alcohols:" by Dr. A. W. Hofmann.

"On the Source of the Water of the Deep Wells in the Chalk under London:" by Dugald Campbell.

"On the Action of Chloride of Cyanogen on Naphthalamine:" by William H. Perkin.

"On some new Colouring Matters, Derivatives of Dinitrobenzol, Dinitronaphthaline, &c. &c.:" by A. Church and W. H. Perkin.

The following Discourses have been delivered during the same period:—

"On the Maintenance of a Permanent Balance between the Animal and Vegetable Kingdoms, in a Medium of Fresh or Sea-water:" by R. Warington.

"On certain Processes recently proposed for the Decomposition of Fats by Water at High Temperatures:" by Dr. A. W. Williamson.

"On the Chemical Statistics of the Animal Body:" by Dr. J. H. Gilbert.

"On the Explosion at Gateshead in October 1854:" by Dr. G. D. Longstaff.

"On some points in the Practice of the Assay of Gold and Silver:" by Dr. W. A. Miller.

"On some new Bases containing Phosphorus:" by Dr. A. W. Hofmann.

"On some Laws of Chemical Combination:" by Dr. J. H. Gladstone.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY. *Cr.*

1855.		£	s.	d.	1856.		£	s.	d.
March 28.	To Balance from last Account	31	15	10½	March 29.	By Payment of One Year's Rent to Polytechnic Institution	120	0	0
1856.									
March 29.	„ Subscriptions since received	302	16	0	„ „	„ Ditto to H. Baillière for Publishing Journal	131	18	6
„ „	„ Admission Fees from Ten New Members	20	0	0	„ „	„ Ditto of One Year's Salary to Editor of Journal	50	0	0
„ „	„ Composition from a Country Member, in lieu of future Subscriptions	10	0	0	„ „	„ Ditto for Books and Periodical Publications	61	15	0
„ „	„ Half-year's Dividend on £300 Three per Cent. Consols, minus Property Tax	4	4	0	„ „	„ Ditto of One Year's Salary to the Librarian	15	0	0
„ „	„ Proceeds of Sale of £150 Three per Cent. Consols, minus Brokerage, Power of Attorney, and Postage	135	4	3	„ „	„ Ditto to the Royal Society for their "Proceedings" sent to the Members of Chemical Society	20	0	0
„ „	„ Rent paid for Use of Rooms by Meteorological Society, Two Years	40	0	0	„ „	„ Ditto for Attendance and for Tea and Coffee	41	15	10
„ „	„ Ditto for ditto from Etnological Society, One Year	20	0	0	„ „	„ Ditto for Petty Cash, Postage Stamps, &c.	6	12	11
„ „	„ Proceeds of Sale of "Memoirs" and of Journal	4	9	8	„ „	„ Ditto to R. Ireland for a Book-case	11	0	0
„ „	„ Ditto of ditto of a Book-case	3	0	0	„ „	„ Ditto to Imperial Gas Company for Gas	1	10	0
					„ „	„ Ditto to Cavendish Society, Subscription 1856	1	1	0
					„ „	„ Ditto for Coals and Wood	1	10	0
					„ „	„ Ditto to the Collector for Poundage	14	12	0
					„ „	„ Balance to his debit in next Account	94	14	6½
		£	571	9 9½			£	571	9 9½

London: 31st March, 1856.

ROBERT PORRETT, Treasurer.

Examined and found correct,

BENJAMIN H. PAUL,
GEORGE SIMPSON,
HENRY M. NOAD,
} Auditors.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

April 7, 1856.

Dr. W. A. Miller, President, in the Chair.

The following donations were announced:—

"The American Journal of Science and Art:" from the Editors.
"The Journal of the Franklin Institute:" from the Institute.
"The Proceedings of the Royal Society:" from the Society.
"The Pharmaceutical Journal:" from the Editor.
"The Journal of the Society of Arts:" from the Society.
"The Journal of the Photographic Society:" from the Society.
"The Literary Gazette:" from the Publishers.
"On the Constitution and Properties of Ozone:" by Thomas Andrews, M.D. From the Author.

The following gentlemen were elected Fellows of the Society:—

Thomas J. Smith, Esq., Whitefriargate-street, Hull;
George Jolly, Esq., 13, Curzon-street, May Fair;
Henry Matthew Witt, Esq., Museum of Practical Geology, Jermyn-street;
Thomas J. Dyke Acland, Esq., Sprydoncote, near Exeter.

The following papers were read:—

"Contributions to the History of Nitric Acid, with especial reference to the Valuation of Nitre (second paper):" by F. A. Abel and C. L. Bloxam.

"On New Methods for the Estimation of Minute Quantities of Nitric Acid and Ammonia:" by J. Thomas Way.

April 21, 1856.

Dr. J. H. GILBERT in the Chair.

Thomas J. Smith, Esq., and A. H. Church, Esq., were admitted Fellows of the Society.

The following donations were announced:—

"The Journal of the Society of Arts:" from the Society.
"The Journal of the Photographic Society:" from the Society.
"The Literary Gazette:" from the Publishers.

James Allan, M.A., Ph.D., of 52, Hanover-street, Sheffield, was elected a Fellow of the Society.

Professor Abel delivered a discourse "On Chemistry as applied to the Manufacturing Branches of the War Department."

May 5, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"The Pharmaceutical Journal:" from the Editor.
"The Journal of the Franklin Institute:" from the Institute.

Alexander Harvey, Esq., of Glasgow, was elected a Fellow of the Society.

Dr. Warren De la Rue made a verbal communication upon "Some Properties of the Metals of the Alkalies."

The following papers were read:—

"Note on a New Method of Making Ferricyanide of Potassium, and a Paracyanogen Compound:" by Lyon Playfair, C.B., Ph.D., F.R.S.

"On the Sulphovinates, and on Amylophosphoric Acid and the Amylophosphates:" by Frederick Guthrie, Ph.D.

May 19, 1856.

Dr. WARREN DE LA RUE, Vice-President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"The Proceedings of the Royal Society:" from the Society.

Samuel Clift, Esq., of Manchester, was elected a Fellow of the Society.

Mr. Alfred Harnett and Mr. John Attfield were elected Associates of the Society.

Dr. W. Odling made a verbal communication upon the "Distribution and General Characters of the Bibasic Organic Acids."

Professor Abel remarked upon some "Circumstances connected with the origin of the late Explosions at Woolwich Arsenal."

"Mr. H. M. Witt described some "Experiments showing the power of Filtering Media to remove the Dissolved Constituents of River Water."

June 2, 1856.

Dr. W. A. MILLER, President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"The Journal of the Photographic Society:" from the Society.
"The Proceedings of the Royal Society:" from the Society.
"The Pharmaceutical Journal:" from the Editor.

The following gentlemen were elected Fellows of the Society:—

William Kay, B.A., Stonyhurst, Whally, Lancashire;
John Hamilton Clements, Esq., 4, Union-court, Old Broad-street.

The following papers were read:—

"On Lophine:" by A. Gössmann and E. Atkinson.
"On the Temperature of the Opposite Sides of a Bismuth Joint

while traversed by a Hydro-electrical Current:" by Richard Adie.—The author's experiments seem to show that the side of a medium at which electricity enters, is of a higher temperature than the side at which the electricity quits the medium. The differences observed were, however, very slight, seldom exceeding half a degree Fahrenheit.

"On the Analysis of a Meteoric Stone from the Desert of Atacama:" by Frederick Field.

"On the Decomposition by Heat of Native Oxichloride of Copper or Atacamite:" by Frederick Field.

June 18, 1856.

Dr. W. A. Miller, President, in the Chair.

The following donations were announced:—

"The Quarterly Journal of the Geological Society:" from the Society.
"The Journal of the Franklin Institute:" from the Institute.
"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"On Electric Induction:" by Professor Faraday and Dr. Riess.

The following pamphlets and publications were presented by the Academy of Sciences at Münich:—

"Denkrede auf Dr. Siber und Dr. Ohm, bei Dr. Lamont."
"Zwei Reden: von F. Thiersch."
"Ein Catalog der Veröffentlichungen, Reden und Verhandlungen der kaiserlichen Akademie."
"Verhandlungen der mathematisch-physicalischen Klasse."
"Gliederung der Bevölkerung Baierns: von Dr. Hermann."
"Almanach der kaiserlichen Akademie der Wissenschaften."
"Ursache der spontanen Bläuung einiger Pilze: von Schönbein, vom Verfasser."

Messrs. Piria, Schrötter, Strecker, and Wurtz, were elected Foreign Members of the Society.

August Dupré, Ph.D., of Deptford, was elected an Associate of the Society.

The following papers were read:—

"On Cadmium-Ethyle:" by J. A. Wanklyn.

"Description of a Self-acting Washing-Bottle:" by William Stephens Clark.

"On a Coal-gas Carbon and Nitric Acid Voltaic Battery:" by James L. and L. Wheeler.

"On the Analysis of the Iron used in English and Foreign Ordnance:" by F. A. Abel.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

On the Constitution and Properties of Ozone.*

By Thomas Andrews, M.D., F.R.S., M.R.I.A.

Among the many interesting bodies which the researches of modern chemists have brought to light, few are more remarkable than the substance to which the name of Ozone has been given, whether we consider its many singular and anomalous properties, or its intimate relations with the most important and widely-diffused element in nature. For the first recognition of ozone and description of its properties, we are indebted to the sagacity of Schönbein, to whom the entire merit of the discovery unquestionably belongs. His earlier experiments were, however, chiefly directed to the elucidation of its properties, and of the conditions under which it is formed; but not being accompanied by quantitative determinations, they did not throw any clear light on its actual constitution. The subject has also attracted of late years the attention of several very distinguished physical and chemical inquirers, among whom I may particularly mention Marignac, De la Rive, Berzelius, Williamson, Fremy and Becquerel, and Baumert.

Schönbein has shown that a body having a peculiar and highly characteristic odour and very similar properties is formed under the three following conditions:—

1. When electrical sparks are passed through atmospheric air.
2. When pure water, or water holding certain acids or salts in solution, is decomposed by the voltaic current, the new substance appearing, along with the oxygen gas, at the positive pole.
3. When certain bodies, and particularly phosphorus, are slowly oxidised at common temperatures in atmospheric air.

Two distinct questions here arise for consideration. Is the same

* Phil. Trans. 1856, I. 3.

substance produced under these different conditions, or has Schönbein included under the name of ozone substances having different compositions, although agreeing in some of their properties? And next, what is the composition of ozone; or, if there be more ozones than one, how are they respectively constituted?

The experiments of Williamson* indicated the production of water, when ozone obtained by electrolysis was decomposed by being passed over heated copper; and Baumert† obtained similar results when he passed a stream of electrolytic oxygen through a tube containing anhydrous phosphoric acid, which was heated at one point to redness. These experiments were not, however, adapted to yield quantitative results, but they led to the general conclusion that this variety of ozone is an oxide of hydrogen containing more oxygen than water. But from another and very important experiment, to which I shall have occasion hereafter very fully to refer, Baumert has concluded that it is a teroxide of hydrogen, HO_3.

On the other hand, the experiments of De la Rive and of Fremy and Becquerel‡ have shown that pure and dry oxygen gas may be converted by the electrical spark into ozone.

I am not aware of any experiments on ozone obtained by the action of phosphorus on atmospheric air, which throw any distinct light on its constitution. Marignac passed a stream of this ozonised air through a solution of iodide of potassium, till the whole of the iodide was converted into iodate of potassa, and concluded that ozone produced in this way must be either oxygen in a peculiar state, or a peroxide of hydrogen.

According to the results, therefore, of the most recent investigations, it would appear—

That the substances comprehended under the name of ozone are not identical;

That the ozone obtained by the action of the electrical spark on oxygen gas is oxygen itself in an altered or allotropic state;

That the ozone obtained by the electrolytic decomposition of water is an oxide of hydrogen, having the formula HO_3; and

That the ozone obtained by the action of phosphorus on oxygen is either oxygen itself, or a compound of oxygen and hydrogen.§

The subject of ozone has at intervals engaged my attention during the last four or five years, and I was actually occupied with a series of experiments on the production of ozone by the electrical spark, when the appearance of Fremy and Becquerel's

* Memoirs of Chemical Society, ii. 395.

† Pogg. Ann. lxxxix. 39.

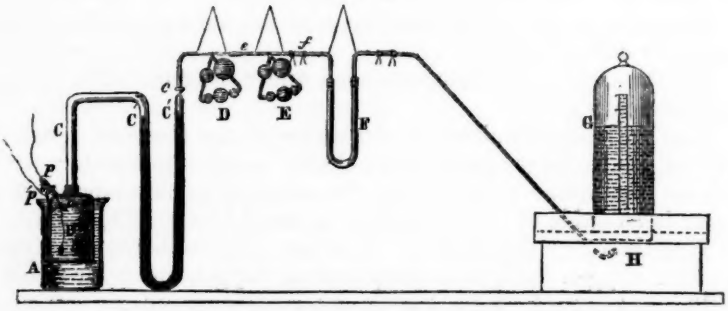
‡ Ann. Ch. Phys. [3] xxxv. 62.

§ For a very complete account of all that is known on this subject, see the article "Ozon" in the "Handwörterbuch der Chemie," v. 835 (Braunschweig, 1853).

able researches induced me for the moment to lay aside the inquiry. The publication of Baumert's memoir led me subsequently to resume it, as his results were not in accordance with those which I had previously arrived at. But the method proposed by that physicist to determine whether ozone is an oxide of hydrogen, or oxygen in an allotropic condition, appeared to be so well suited to the purpose, that on resuming the inquiry I considered it necessary, in the first instance, carefully to repeat his experiments. The results which I at first obtained were so far in accordance with those of Baumert, that they showed that the increase in weight of the apparatus was always more than the weight of the ozone, as deduced from its chemical action, but the relative proportion of these quantities was not in accordance with his results; nor, on repeating my own experiments, did they agree with one another. It was evident, therefore, that some disturbing cause existed which complicated the reaction, and, on further investigation, I not only found that such a cause did really exist, but succeeded in ascertaining its nature and the means of avoiding it. The experiments, on being now repeated, gave results very consistent with one another, and altogether at variance with the view that hydrogen is a constituent of ozone.

The apparatus which I employed was arranged as follows:—A is a vessel (Plate I. Fig. 1) of about two litres capacity, containing a mixture of one measure of pure and strong sulphuric acid and seven measures of distilled water. The cylinder B, which

FIG. 1.



is filled with a similar solution, is closed below with a diaphragm of bladder, so as to prevent effectually any mixture of the gases evolved at the two poles. A platina wire, *pp*, traverses and is fused into a short glass tube, fitted by grinding into the tubulated neck *b*: this wire terminates below in a bunch of fine platina wires, which form the positive pole of a voltaic arrangement. The negative pole is a platina plate, *p'*, immersed in the liquid of the outer vessel. The vessel A was placed in a larger vessel containing cold

water, to which ice was in some experiments added. This vessel has been omitted in the drawing for the sake of distinctness. CC′C″ is a continuous tube, united by fusion with the larger neck of B, and filled from C′ to C″ with fragments of pumice, moistened with pure sulphuric acid. The length of the desiccating column was nearly one metre. D is a Liebig's apparatus, to the ends of which glass tubes were fused, which had previously been fitted by grinding, the one into the neck *c* of CC′C″, the other into a tube which was in like manner fused to a second Liebig's apparatus, E. The connections *c* and *e* were, therefore, formed by glass surfaces carefully ground. In my earlier experiments these connections were made by means of small and dry corks, which, on the whole, are more convenient than ground-glass joints, and are quite unobjectionable, as, when the surface is small and the cork dry, the amount of ozone destroyed by contact with the cork is wholly inappreciable. Caoutchouc connectors of any kind are altogether inadmissible; they are attacked with such energy by ozone, even when diluted with 1000 times its volume of other gases, that the tube becomes perforated in the course of a few minutes. The vessel D contained a solution of iodide of potassium acidulated with a little hydrochloric acid, and the vessel E concentrated sulphuric acid. The U-tube F, filled with pumice moistened with sulphuric acid, prevented any moisture from passing backwards into E. The oxygen evolved was collected in the graduated glass vessel G, inverted over water. The volume of the oxygen gas was determined only for the purpose of ascertaining its relation to the ozone produced.

The mixture of oxygen and ozone, having been perfectly desiccated in its passage through the long tube CC′C″, enters the vessel D, where the ozone is decomposed, iodine being set free and caustic potassa formed, which latter, combining with the free hydrochloric acid, forms chloride of potassium. If a neutral solution of iodide of potassium is employed, the reaction is more complicated; for, while the greater part of the iodine is set free as before, and dissolves in the excess of iodide of potassium, iodate of potassa and caustic potassa are at the same time formed. Whether the solution be taken in an acid or neutral state, the final result is in this respect always the same, that the active oxygen enters into a chemical combination in the vessel D, and increases the weight of the liquid contained in that vessel.

The increase in weight of the vessels D and E will give the entire weight of the ozone, whether that body be allotropic oxygen or an oxide of hydrogen. On the former supposition, the decomposition of the iodide of potassium will result in the substitution of oxygen for iodine, both remaining in D, while the sulphuric acid in E will retain the moisture which would otherwise be swept away by the

current of dry gas; on the latter, ozone will become resolved into water and oxygen, both of which will be retained in the vessels D and E. Now by determining the amount of free iodine in the iodide of potassium solution at the end of the experiment, the amount of active oxygen by which it has been displaced may be easily calculated; and on comparing this with the increase in weight of the vessels D and E, it will at once be seen whether ozone be a peroxide of hydrogen yielding water in its decomposition.

Two experiments of this kind were performed by Baumert: in the first, the increase in weight of the apparatus amounted to 0·0133 grm., and the weight of the oxygen, as calculated from the iodine set free, to 0·0081 grm.; in the second, the same quantities were respectively 0·0149 grm. and 0·00989 grm. The iodide of potassium was employed in the state of a neutral solution, and the iodate of potassa was subsequently decomposed by the addition of a little hydrochloric acid.

It was from these results that Baumert inferred that the ozone which accompanies oxygen obtained by the electrolysis of water, is an oxide of hydrogen having the formula HO_3; and this conclusion, deduced from experiments which were devised with great skill and executed with care, has, in Germany at least, received very general assent.

Having, as already mentioned, found, on a repetition of these experiments, that a different expression resulted for the composition of ozone from every new trial, I instituted a diligent search into all the circumstances of the experiment, and at last succeeded in referring the irregularities to the presence of a small but appreciable quantity of carbonic acid, which, unless very great precautions be taken, is always present in electrolytic oxygen. When baryta-water was substituted for the solution of iodide of potassium in D, a precipitate of carbonate of baryta appeared in the course of a few minutes. With caustic potassa in the same vessel, the increase in weight for the same volume of oxygen gas was considerably greater than with the solution of iodide of potassium, and at the end of the experiment it was found that carbonate of potassa had been formed. Now as a small quantity of free potassa is always produced during the action of ozone on a neutral solution of iodide of potassium, it appeared not improbable that this would seize upon a portion of the carbonic acid just referred to, and thus the augmentation in the weight of the apparatus would depend upon two distinct causes,—the ozone reaction, and the absorption of carbonic acid. To prevent the occurrence of the latter, it was only necessary to acidulate the solution of iodide of potassium, so as to prevent the formation of free potassa, or to boil for some time the liquid subjected to electrolysis. The acidulation of the solution alone was found to be sufficient to prevent the carbonic

acid from being absorbed: for when this precaution was attended to, the results were the same, whether the electrolyte was boiled immediately before the commencement of the experiment or not. With this modification, the irregularities previously observed in different trials disappeared, and the simple and interesting result was obtained, that the increase in weight of the apparatus was exactly equal to the amount of oxygen deduced by calculation from the iodine set free.

I will now describe the chief precautions which I adopted to avoid, as far as possible, all sources of error in the following experiments, the delicacy of which will at once be apparent, if we consider that not more than 40 milligrammes of ozone are contained, under the most favourable circumstances, in 10 litres of electrolytic oxygen; and that it was necessary to have the arrangements so perfect, that this large quantity of gas (supposed to be free from ozone) should traverse the apparatus without producing any appreciable change in the united weight of the vessels D and E.

The solution of iodide of potassium employed in all the experiments had the same composition, although the quantity of ozone obtained in some cases was three times greater than in others. It consisted of 2 grms. of iodide of potassium dissolved in 22½ grms. of a weak solution of hydrochloric acid, containing 2 per cent. of pure acid. As it is difficult to procure iodide of potassium entirely free from iodate of potassa, I always prepared, at the commencement of each experiment, two similar solutions, of which one was introduced into D, and the other preserved in a ground-stoppered vial, till the experiment was finished. The amount of free iodine in both was determined at the same time, and the difference taken to represent the exact quantity of iodine due to the ozone reaction. The correction for the iodate of potassa in the original solution, when reduced, rarely represented more than 0·001 grm. oxygen, but quantities of this magnitude must not be neglected in these experiments.

Previous to weighing the vessels D and E, one litre of atmospheric air, deprived of carbonic acid and carefully desiccated, was passed through the apparatus. The object of this precaution was to bring every part of the apparatus into the same state, at the beginning of the experiment, in which it would be at the end. The same volume of dry air was passed through the apparatus at the conclusion of each experiment.

It is rarely necessary in chemical investigations to apply a correction to the direct indications of the balance for changes in the temperature and pressure of the atmosphere, during the interval between two successive weighings. By preserving the apartment at a pretty uniform temperature, the corrections for thermometric changes may be confined within very narrow limits; but the

movements of the barometer are not under our control; and when, as in these experiments, a period of two and sometimes of three days elapsed between the first and second weighings, it occasionally happened that the change in the atmospheric pressure was considerable, and an appreciable error (amounting in some instances to nearly 0·002 grm.) would have occurred, if no correction had been applied.*

To ascertain how far the action of the apparatus might be relied on, one or two preliminary experiments were made, which gave very satisfactory results. The vessel D, containing pure water,—E, sulphuric acid,—and another Liebig's condenser also containing sulphuric acid, having been interposed between E and F, 3·5 litres of oxygen gas not containing ozone, followed by 1 litre of atmospheric air, were passed through the apparatus. The time occupied in the passage of the gas was about five hours. The vessel D lost 0·0311 grm., while E gained 0·0315 grm., the third vessel not sustaining any appreciable change of weight. If, therefore, D and E had been weighed together, the change of weight would have been only 0·0004 grm. In another experiment, in which a solution of strong caustic potassa was placed in D, the loss of D was 0·0175 grm., and the gain of E 0·0172 grm., the difference being less than one-third of a milligramme. Other experiments of the same kind, with different solutions in D, gave similar results. It is evident, therefore, that at the rate at which the gas traversed the apparatus, the whole of the moisture carried off from the liquid in D was retained by the sulphuric acid in E.

To determine whether a notable quantity of iodine would be carried over by the current of the gas from D to E, a solution of iodide of potassium containing a large quantity of free iodine was introduced into D, and a solution of pure iodide of potassium into E. After passing 4 litres of air through the apparatus, E was found to contain 0·0015 grm. iodine. This is equivalent to one-tenth of a milligramme of oxygen, and, from the large excess of iodine

* This correction was calculated as follows :—To the volume in cubic centimetres of the solution of iodide of potassium in D, and of sulphuric acid in E, was added the volume of the glass of which the vessels D and E were formed. From this was deducted the volume of the weights employed. Let v be the difference of the volumes so found in cubic centimetres; p and p', the atmospheric pressures in English inches at the first and second weighings; t and t', the corresponding temperatures in Centigrade degrees; x, the weight in grammes of a volume of air equal to v, measured under the pressure p, and at the temperature t; x', the weight of the same volume of air at p' and t'. Then, since 1 cub. cent. air at 0°, and under a pressure of 29·92 inches, weighs 0·00129 grm.,

$$x' - x = \mathrm{v}\left(\frac{1}{1 + 0{\cdot}00367\,t'} \cdot \frac{p'}{29{\cdot}92} - \frac{1}{1 + 0{\cdot}00367\,.t} \cdot \frac{p}{29{\cdot}92}\right) \cdot 0{\cdot}00129.$$

The value of $x' - x$ is to be added to, or subtracted from, the increase of weight, as found by direct experiment, according as it is a positive or negative quantity.

in the first solution, must be a greater quantity than could have been carried over in any of the subsequent experiments, although in some of them larger volumes of gas were passed through the apparatus.

The free iodine was determined according to the very delicate method first, I believe, proposed by Bunsen. A dilute solution of sulphurous acid was prepared, and its strength determined, immediately before analysing the liquid in D, by ascertaining how many measures of it were required to destroy a known weight of free iodine in a solution of iodide of potassium. A corresponding experiment was made with the solution in D, from which the quantity of free iodine in it was deduced by a very simple calculation.

I. 10·2 litres of electrolytic oxygen containing ozone were passed through the apparatus at the rate of about three-quarters of a litre per hour. At the first weighing, the barometer was 29·85 in., and the thermometer 5°·9 C.; at the second weighing, the barometer was 29·98 in., and the thermometer 5°·3. The value of V (see preceding note) was 47 cub. cent. The gain in weight of the double apparatus D and E was 0·0375 grm., which gives, when corrected for atmospheric changes, for the true gain, 0·0379 grm. The free iodine in the solution contained in D was neutralised by 112·7 measures of a dilute solution of sulphurous acid. The other solution of iodide of potassium, which had been prepared at the same time as the first, and to which the same amount of acid had been added, required 0·8 measure of the same solution of sulphurous acid for neutralisation. Hence the iodine eliminated by the action of the ozone was equivalent to 111·9 measures. Next, 0·5341 grm. pure iodine was added, together with 2 grms. of iodide of potassium, to a few drops of water, and when both were dissolved, the solution was diluted till it occupied exactly 100 cub. cent. From the mean of two experiments which closely agreed with one another, it appeared that 100 measures of the solution of sulphurous acid neutralised 95·96 cub. cent. of this solution, and hence 1 measure of the former corresponded to 0·00512 grm. iodine. From these data it follows, by an easy calculation, that the iodine disengaged by the ozone amounted to 0·609 grm., and the equivalent of oxygen to 0·0386 grm.

II. 2·72 litres of electrolytic oxygen were passed through the apparatus at the same rate as before. At first weighing, barometer 29·60 in., thermometer 5°·8 C.; at second weighing, barometer 29·60 in., thermometer 6°·0 C. Gain of weight of D and E 0·0107 grm.; corrected, 0·0107 grm. The free iodine in D, after deducting the iodine due to the small quantity of iodate of potassa in the original solution, was neutralised by 30·23 measures of a solution of sulphurous acid, of which, as ascertained by direct ex-

periment made at the time, 1 measure neutralised 0·00521 grm. free iodine. Hence the oxygen due to the displacement of iodine was 0·0100 grm.

III. 2·86 litres of the same gas as in the preceding experiments were passed through the apparatus. At first weighing, barometer 30·06 in., thermometer 6°·6 C.; at second weighing, barometer 30·20 in., thermometer 6°·1 C. Gain of weight of D and E 0·0152 grm.; corrected, 0·0154 grm. The free iodine in D, corrected as before, was neutralised by 41·52 measures of a solution of sulphurous acid, of which 1 measure neutralised 0·00525 grm. iodine: hence the weight of oxygen, as deduced from the weight of iodine set free, was 0·0138 grm.

IV. 6·45 litres of electrolytic oxygen were passed through the apparatus. At first weighing, barometer 29·96 in., thermometer 6°·8 C.; at second weighing, barometer 29·29 in., thermometer 7°·8 C. Gain of weight of D and E 0·0303 grm.; corrected, 0·0288 grm. The free iodine in D was neutralised by 100·4 measures of a solution of sulphurous acid, of which 1 measure neutralised 0·00441 grm. iodine: hence the weight of oxygen deduced in this way was 0·0281 grm.

V. 6·8 litres of electrolytic oxygen passed. At first weighing, barometer 30·53 in., thermometer 9°·8 C.; at second weighing, barometer 30·44 in., thermometer 10°·4 C. Gain of weight of D and E 0·0254; corrected, 0·0251 grm. The free iodine in D neutralised 107·9 measures of a solution of sulphurous acid, of which 1 measure was equivalent to 0·00358 grm. iodine: hence the weight of oxygen deduced from the iodine set free was 0·0273 grm.

Collecting these results, and adding them together, so as to obtain the mean of the whole, we have

	Ozone deduced from the increase in weight of the apparatus.	Ozone deduced from the iodine liberated.
I.	0·0379 grm.	0·0386 grm.
II.	0·0107 grm.	0·0100 grm.
III.	0·0154 grm.	0·0138 grm.
IV.	0·0288 grm.	0·0281 grm.
V.	0·0251 grm.	0·0273 grm.
	0·1179 grm.	0·1178 grm.

The agreement is complete, and proves unequivocally that water is not a product of the decomposition of ozone, which therefore does not contain hydrogen as a constituent. If its composition were HO_3, the apparatus would have increased 0·1841 grm. in weight, instead of 0·1179 grm.

The amount of ozone formed in these experiments was tolerably

uniform. For 1 litre of oxygen the following weights of ozone were obtained:—

I.	0·0038 grm.
II.	0·0037 grm.
III.	0·0046 grm.
IV.	0·0043 grm.
V.	0·0040 grm.
Mean . .	0·0041 grm.

In the arrangement above described, the oxygen gas derived from the electrolytic decomposition of water was therefore accompanied by about $\frac{1}{350}$th of its weight of ozone.

In order to remove every possible doubt from these results, I fitted up an apparatus from every part of which organic substances were excluded. No diaphragm was used, and all the connexions were made either by fusing the ends of the connecting tubes together, or by means of ground-glass joints. The arrangement is represented in Fig. 2. Two platina wires (Fig. 3) were fused into the end of a glass tube, which was fitted by grinding to the tubulated neck *b* of the vessel A. The tube BB′B″ was connected at *a*

FIG. 2.

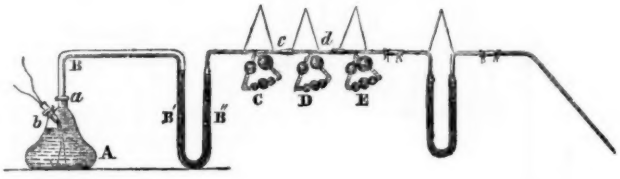


FIG. 3.

with the vessel A by a ground joint, and with C by fusion. It contained pumice moistened with sulphuric acid. The vessel C was also filled with sulphuric acid, and was connected by a ground glass joint with the iodide of potassium vessel D. The vessel E contained, as before, sulphuric acid. In this experiment, both the hydrogen and the oxygen traversed the apparatus, the accuracy of which was thus exposed to a very severe test.

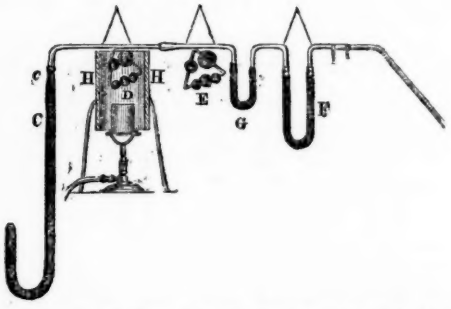
Twenty-two litres of the mixed gases were passed through the apparatus. The gain in weight of D and E was 0·0135 grm., the respective heights of the barometer at the first and second weighings having been 28·96 in. and 29·57 in., and the temperatures 11°·1 and 10°·0. The correction for change of pressure and temperature is therefore +0·0014 grm., and the true gain 0·0149 grm. The free iodine in D, due to the action of the ozone, neutralised 62·65 measures of a solution of sulphurous acid, of which 1 mea-

sure corresponded to 0·00373 grm. iodine. The weight of ozone deduced from the iodine set free is therefore 0·0148 grm.

The identity of these results is very satisfactory, when it is considered that this small weight of ozone was separated from 22 litres, or nearly five gallon measures of the mixed gases. The relative quantity of ozone to the amount of water decomposed is less than in the former experiments, arising perhaps partly from a single platina wire having been in this case employed as the positive pole. In this experiment, great care was taken to exclude both carbonic acid and nitrogen from the electrolyte.

My next object was to determine, by careful quantitative experiments, whether water is really formed, as Williamson and Baumert have stated, when ozone is decomposed by heat. For this purpose, the same general arrangement was employed as in the first series of these experiments; but the first Liebig's apparatus D, instead of being filled with a solution of iodide of potassium, was now empty, and placed in the upper part of a metallic cylinder (Fig. 4, HH), where it was raised to a temperature of about

Fig. 4.



400° C., by a current of heated air from a Leslie's burner. To the sulphuric acid apparatus E was permanently attached, and weighed along with it, a small U-tube G, containing anhydrous phosphoric acid, so as to secure the condensation of the last trace of aqueous vapour, if any were present. The oxygen gas was collected and measured as in the former experiments.

Two experiments were made. In the first, 6·8 litres of oxygen containing 0·027 grm. ozone were passed through the apparatus; in the second, 9·6 litres containing 0·038 grm. ozone. The compound sulphuric and phosphoric acid apparatus was found, all corrections having been made, to have increased, in the one case one-third, and in the other case one-half of a milligramme in weight. Such quantities can only be referred to the unavoidable errors of experiment. If ozone were a compound body having the constitu-

tion HO_3, the apparatus would have gained in the first experiment 10, and in the second 14 milligrammes.

That ozone cannot contain nitrogen will appear from the following experiment. Two platina wires were hermetically sealed into the bottom of a small flask, into which water, containing a little sulphuric acid, was introduced, and made to boil rapidly for some time. While the water was in a state of ebullition, the wires were connected with the poles of a voltaic arrangement, so as to disengage the mixed gases along with the vapour of water. So long as the ebullition continued, no ozone made its appearance; but on allowing the liquid gradually to cool, without arresting the current, its presence soon became manifest from its odour and action on iodide of potassium paper. The ebullition and the current of the mixed gases must have rendered the presence of nitrogen here impossible.

One question still remains to be answered. Does ozone, besides oxygen, contain any other constituent which is not absorbable by any of the reagents employed? Although the gas which escaped from the apparatus, after the separation of the ozone, appeared to be pure oxygen, yet it would be rash to assert that it might not have contained some unknown body amounting to $\frac{1}{1000}$th of its weight, and having no very salient properties. This question appeared to me to admit of solution in another way. It will be seen, in a subsequent part of this paper, that there can be no doubt of the formation of ozone from pure and dry oxygen by the action of the electrical spark; and nothing is easier than to convert the whole of a given volume of oxygen into ozone in presence of a solution of iodide of potassium. The next step in the inquiry was, therefore, to ascertain whether ozone derived from electrolysis, from the action of the electrical spark, and from the oxidation of phosphorus, exhibited a perfect identity in all its properties.

One of the most remarkable properties of ozone is its destruction by heat, or rather its conversion by heat into ordinary oxygen. To ascertain the temperature at which this change occurs, the vessel D, Fig. 4, was placed in a bath of mercury, and the gas examined as it escaped, without previously passing it through the rest of the apparatus. On heating the mercurial bath, the amount of ozone, as determined by its action on iodide of potassium paper,* did not notably diminish till the temperature attained 230° C. It still continued, however, very intense till the thermometer rose to 235°. Between that point and 240°, the ozone reactions entirely disap-

* Bibulous paper which has been dipped into a solution of iodide of potassium of moderate strength, and afterwards allowed to dry, but still retaining its hygrometric moisture, is the most convenient test of ozone. If it be exposed to a continuous current of dry air, it should be removed from time to time, and its hygrometric moisture restored.

peared, when the ozone was in a very dilute state; but when more concentrated, slight traces of ozone could still be discovered, which no doubt would have also disappeared if the current of gas had been passed very slowly. Time is, in fact, an element in this action. Even at the temperature of 100° C. ozone is slowly destroyed. Two similar tubes were filled at the same time, and by the same process, with ozone diluted as usual with oxygen, and afterwards hermetically sealed. One of these tubes was maintained for three hours in a vapour bath at 100° C., the other was not exposed to heat. On examining both tubes at the end of the time, it was found that the ozone in the tube which had been exposed to heat was perceptibly less than in the other. I have no doubt that, even at the common temperature of the air, ozone preserved in an hermetically sealed glass tube would gradually change into common oxygen. I made an experiment of this kind two or three years ago, which resulted in the disappearance of the ozone; but I do not remember the source from which the ozone was derived, nor what precautions were taken to dry the gas.

On the other hand, ozone brought directly into contact with the vapour of water at the boiling point is instantly destroyed.

To obtain a continuous stream of ozone from the action of the electrical spark, a current of pure oxygen gas, obtained from the decomposition of the chlorate of potassa, and purified and dried by passing through tubes containing hydrate of potassa and sulphuric acid, was exposed to a rapid succession of electrical sparks. To obtain a sufficient stream of electricity, an electrical machine, firmly screwed down to the floor of the apartment, was connected by a belt with a heavy cast-iron wheel, 40 inches in diameter, contained in a frame which was also firmly secured to the floor. By this arrangement, the machine could be worked for any length of time continuously, the plate performing about 360 revolutions per minute. It was of course necessary to apply very frequently a hand rubber covered with amalgam to the plate, and it required the co-operation of three persons to permit the work to be easily performed. On passing the gas through the apparatus at nearly the same rate as in the experiments already described, an abundant stream of ozone was obtained, which enabled me to institute a very exact comparison between its properties and those of ozone obtained by electrolysis.

When heated in the mercurial bath, ozone prepared in this way was rapidly destroyed at the temperature of 237° C., which is the same temperature at which electrolytic ozone was also destroyed. The vapour of boiling water, in like manner, caused all the ozone reactions to disappear.

The action of water at common temperatures and of alkaline solutions upon ozone is very remarkable. It is commonly stated

that caustic potassa absorbs ozone, but that pure water, and solutions of lime, baryta, and ammonia, have no action upon it. This statement is far from being accurate. Pure water does not absorb ozone, and a stream of air containing ozone may be passed for any length of time through water without producing any change in the properties of the water. I have also preserved ozone for several days in a stoppered vial containing a little distilled water, and, although the vessel was agitated from time to time, the ozone did not disappear. On the other hand, pure water has the property of destroying a small quantity of ozone. If ozone, obtained by the electrolysis of water, or by the action of the electrical spark, or by means of phosphorus, be largely diluted with atmospheric air, it will entirely disappear, if an attempt be made to collect it in a jar inverted over water. The following experiment is more precise:—A flask provided with a ground glass stopper, of the capacity of half a litre, was filled with equal volumes of water and atmospheric air, and inverted in the pneumatic trough. The ozone in a single bubble of electrolytic oxygen, passed quietly through the water into this volume of air, could easily be detected; but on agitating the water briskly, even four or five bubbles were deprived of their ozone. The same gas, agitated with twice its volume of lime-water, or one-third of its volume of baryta-water, also ceased to exhibit the reactions of ozone. In like manner, the action of caustic potassa is also limited. A strong solution of that alkali in a Liebig's apparatus deprived one litre of electrolytic oxygen of its ozone, after which the ozone passed freely through it. These phenomena are singular and characteristic, and are the same with ozone, from whatever source it is derived.

Peroxide of manganese destroys ozone, affording an interesting example of what is commonly called catalytic action. The oxide of manganese does not increase in weight, nor is water formed. Ozone from the three sources gives the same results.

The odour of ozone, from whatever source derived, is the same. The same remark applies to its property of bleaching, without producing at first an acid reaction.

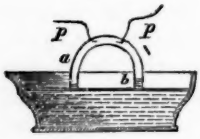
Iodide of potassium is decomposed, with the formation of iodate of potassa; and oxidable substances in solution, as the protosulphate of iron, are raised to a higher state of oxidation by all the varieties of ozone.

It would not be difficult to extend this comparison, but enough has been shown, I conceive, to establish the absolute identity in properties of ozone, in whatever way it may be prepared. Any difference which, on a superficial examination, may appear to exist, will be found on further inquiry to arise from the ozone being in a more or less dilute state.

That ozone is formed by the action of the electrical spark on

perfectly dry oxygen, is placed beyond all doubt by the following experiment:—The curved tube *a*, Fig. 5, having two platina wires, *pp'*, hermetically sealed into it, was inverted over mercury and carefully filled with pure oxygen, after which a little sulphuric acid was introduced into one end (*b*). The whole was allowed to remain for twenty-four hours, when the oxygen was considered to be perfectly dry. Electrical sparks were now passed for some time between the platina wires, after which a solution of iodide of potassium was introduced into the other end of the tube. It became immediately coloured from the formation of free iodine, and the colour continued slowly to increase as the ozone was gradually absorbed.

Fig. 5.



Again, a solution of iodide of potassium may be made to absorb the whole of the oxygen in a narrow tube, by the passage of electrical sparks. This experiment has been described by Fremy and Becquerel, and I have myself repeatedly verified its accuracy. With a thermometer tube 2 inches long, the whole of the oxygen may be made to disappear in the course of one minute. The solution becomes always red from the decomposition of the iodide of potassium.

We have already seen that neither hydrogen nor nitrogen can be constituents of ozone, whether it be obtained from electrolysis, or from the action of the electrical spark on oxygen; and further, that all the supposed varieties of ozone exhibit in all respects identical properties.

Connecting all these facts together, it clearly follows—

That no gaseous compound having the composition HO_3 is formed during the electrolysis of water; and

That ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition.

On the Formation and Preparation of Formic Acid.

By M. Berthelot.

I. *Formation from Carbonic Oxide.**—The relation of carbonic oxide to formic acid is, in a certain sense, the same as that of olefiant gas to alcohol:

$$C_2H_2O_4 = C_2O_2 + 2HO; \qquad C_4H_6O_2 = C_4H_4 + 2HO;$$

* Compt. rend. xli. 955; Ann. Pharm. xcvii. 135.

alcohol heated with strong sulphuric acid yields olefiant gas; and formic acid similarly treated yields carbonic oxide. Guided by these considerations, Berthelot endeavoured to prepare formic acid from carbonic oxide by a process analogous to that by which he had previously formed alcohol from olefiant gas.* The mode of proceeding adopted was to expose caustic potash to the action of carbonic oxide at a high temperature. 10 grammes of slightly-moistened hydrate of potash are introduced into 4 flasks of about half a litre in capacity; and the flasks filled with carbonic oxide, then sealed, and heated for 70 hours in the water-bath. On subsequently opening the flasks under mercury, the mercury fills them completely, showing that all the carbonic oxide has been absorbed; and on dissolving the contents of the flasks in water, supersaturing with sulphuric acid, and distilling, a distillate is obtained containing dilute formic acid.

II. *Preparation from Oxalic Acid.*†—Gay-Lussac showed that formic acid is produced in the decomposition of oxalic acid by heat, its formation resulting from the union of carbonic oxide and water in the nascent state:

$$C_4H_2O_8 = C_2O_2 + H_2O_2 + 2\,CO_2.$$

The quantity of formic acid thus obtained is, however, very small. But Berthelot has lately found that the whole of the carbonic oxide liberated by the decomposition of the oxalic acid may be made available for the production of formic acid, if the oxalic acid be mixed with glycerine, which appears in this case to act merely by contact. A mixture of 1 kilogramme of commercial oxalic acid, 1 kilogramme of syrupy glycerine, and 100 to 200 grammes of water, is introduced into a retort of 2 litres capacity, and gently heated, the temperature not being allowed to rise much above 100° C. Carbonic acid is then evolved with brisk effervescence, and in 12 to 15 hours, the whole of the oxalic acid is decomposed, half of its carbon being eliminated in the form of carbonic acid. A small quantity of water containing formic acid distils over, and the residue in the retort consists of glycerine containing nearly all the formic acid in solution. To separate the formic acid, half a litre of water is poured into the retort, and the liquid continuously distilled, the water being renewed as it evaporates, till about six or seven litres of liquid have passed over, containing in fact nearly the whole of the formic acid. The residual glycerine may be used in the same manner to convert fresh quantities of oxalic acid into formic. 3 kilogrammes of oxalic

* See Chem. Soc. Qu. J. viii. 148.
† Compt. rend. xlii. 447; Ann. Pharm. xcviii. 139.

acid yielded by this process 1·05 kil. formic acid. According to the equation:

$$C_4H_2O_8, 4\,HO = C_2O_4 + 4\,HO + C_2H_2O_4,$$

the quantity should be 1·09 kil. The formic acid thus prepared is quite pure, and free from oxalic acid.

It is important that the decomposition of the oxalic acid be not too much hurried. If the temperature of the contents of the retort rise too high, a more rapid evolution of carbonic acid takes place at first; ceasing, however, after a while. The temperature then quickly rises to 190°—200°, and a new evolution of gas commences, consisting of carbonic oxide. The liquid which distils over under these circumstances contains of course much less formic acid than would be obtained from the same quantity of oxalic acid, if slowly decomposed. This evolution of carbonic oxide proceeds from the decomposition of the formic acid dissolved in the glycerine (like ammonia in water). Pure formic acid also, when heated to 200°—250° for some hours in closed vessels, is for the most part resolved into water and carbonic oxide gas. To obtain carbonic oxide from oxalic acid, Berthelot heats the oxalic acid mixed with glycerine, and collects separately the carbonic oxide which is evolved, when the heating is continued after the evolution of carbonic acid has ceased.

Chemical Notices.*

By H. Limpricht.

1. *Thioformic Acid*, $C_2H_2\left\{\begin{matrix}S_2\\O_2\end{matrix}\right.$.—When dry sulphuretted hydrogen gas is passed over formiate of lead at a temperature above 100°, for the purpose of preparing formic acid, the resulting acid has a disagreeable alliaceous odour, and not unfrequently small needle-shaped crystals separate from it. These crystals are obtained in greatest quantity when the decomposition of the salt is performed in a tubulated retort, which during the operation is heated to 200°—300° by placing hot coals under it. The formic acid sometimes solidifies after a while in the receiver from separa-

* Ann. Pharm. xcvii 363.

tion of these crystals, and the liquid filtered from them yields after distillation a nearly equal quantity of the same product. If the crystals, after washing with cold water and drying over sulphuric acid, are not quite colourless, they may be recrystallised from alcohol; but the quantity of alcohol required for the purpose is very large. The product obtained from a pound of formiate of lead amounts to only a few grammes.

The amount of sulphur in the crystals was found by analysis to be 51·2 and 52·5 per cent. The formula $C_2H_2S_2O_2$ requires 51·6.

The formation of thioformic from formic acid may be represented by the equation,

$$C_2H_2O_4 + 2\,HS = C_2H_2S_2O_2 + 2\,HO.$$

Thioformic acid crystallises from formic acid, or from boiling alcohol, in slender needles, melts at about 120°, and sublimes, even at a low temperature, in small transparent crystals. It has a faint alliaceous odour, is insoluble in water, dissolves with tolerable facility in alcohol and ether at the boiling heat, but scarcely at all in the cold; a portion of it volatilises, together with the alcohol-vapours.

Strong sulphuric acid dissolves thioformic acid at a gentle heat, with evolution of sulphurous acid and separation of sulphur; strong hydrochloric acid has no action upon it, even at a boiling heat; nitric acid decomposes it readily when heated, oxidising the sulphur to sulphuric acid; strong acetic acid dissolves it in small quantity at a boiling heat, but deposits it again on cooling. When thioformic acid is heated with dilute sulphuric acid and peroxide of lead, the latter assumes a lighter colour; with chromate of potash and dilute sulphuric acid, it forms sesquioxide of chromium. Fused with hydrate of potash, it forms a reddish-yellow mass, which, when treated with dilute sulphuric acid, gives off sulphuretted hydrogen and an odour of garlic. Solution of potash dissolves it but sparingly, even at the boiling heat; and the solution treated with acids gives off traces of sulphuretted hydrogen. Thioformic acid is not soluble in sulphide of ammonium, either in the cold or at a boiling heat.

The alcoholic solution of thioformic acid has no reaction upon litmus; it is not altered by sesquichloride of iron; forms with acetate of lead a yellowish precipitate, which turns black when heated with the liquid; with nitrate of silver it yields an amorphous precipitate, which is white at first, but soon turns black, and dissolves partially in hot water, with separation of metallic silver or sulphide of silver. In consequence of its great proneness to decomposition, the silver-compound could not be obtained in a form adapted for analysis.

2. *Anisoic Acid,* $C_{20}H_{18}O_{12}$.

It is generally supposed that when oil of aniseed is acted upon by nitric acid, anisic aldehyde or anisylous acid and oxalic acid are formed in the first instance, according to the equation

$$\underbrace{C_{20}H_{12}O_2}_{\text{Anisoin.}} + 12\,O = \underbrace{C_{16}H_8O_4}_{\text{Anisic aldehyde.}} + \underbrace{C_4H_2O_8}_{\text{Oxalic acid.}} + 2\,HO.$$

The following experiments, however, render it probable that the first product of the action is a new acid,—anisoic acid:

$$C_{20}H_{12}O_2 + 6\,HO + 4\,O = C_{20}H_{18}O_{12};$$

and that this acid, when subjected to the further action of heat, yields anisic aldehyde and oxalic acid.

When oil of star-aniseed is heated with nitric acid of sp. gr. 1·2 till it sinks to the bottom, and then shaken up with a warm solution of bisulphite of soda, the aqueous solution yields on cooling, not sulphite of anisic aldehyde and sodium, but a soda-salt composed of $C_{20}H_{17}NaO_{12}$, viz., anisoate of soda. The acid of this salt has hitherto been obtained only from oil of star-aniseed; but it would doubtless be also produced from the other oils which contain anisoïn (viz., oil of aniseed, fennel, and taragon).

Anisoic acid, when separated from its silver or barium-salt by hydrochloric or sulphuric acid, crystallises by evaporation of its aqueous solution, in small laminæ; but a concentrated solution left for some time in contact with the air deposits tolerably thick tables. The acid dissolves very readily in water, alcohol, and ether, and is therefore difficult to obtain in good crystals; it has a strong acid reaction, and melts at about 120° C. Heated on platinum-foil, it turns brown, gives off empyreumatic vapours having the odour of anisic aldehyde, and finally burns with a luminous flame. It cannot be sublimed without decomposition, even by careful heating.

A solution of the silver-salt, mixed with hydrochloric acid, having been accidentally left over the fire, together with the precipitated chloride of silver, till it had gone to dryness, a sublimate of white needles was found to have collected on the chloride of silver: these needles had the appearance of anisic acid, and the analysis of their silver-salt showed that they really consisted of that acid. An attempt to obtain anisic acid by heating free anisoic acid moistened with sulphuric or hydrochloric acid, did not succeed, only the empyreumatic decomposition-products being obtained, which anisoic acid yields when heated by itself.

Anisoate of Soda, $C_{20}H_{17}NaO_{12}$ (dried at 100°).—The salt pre-

pared as above, and purified by repeated crystallisation from hot water, forms perfectly white, indistinct crystals united in nodules. It dissolves readily in water. The analysis gave 8·9 per cent. sodium, agreeing exactly with the formula.

Anisoate of Baryta, $C_{20}H_{17}BaO_{12}$ (dried at 100°).—Prepared by mixing the solution of the soda-salt with the quantity of sulphuric acid exactly sufficient to decompose it; evaporating to dryness over the water-bath; exhausting the residue with absolute alcohol, and digesting the solution (mixed with water) with carbonate of baryta till it was neutralised, the filtered liquid yielded by evaporation easily soluble crystalline nodules resembling the soda-salt.

		Calculated.		Found.
20 C	. . .	120	39·8	39·23 to 39·65
17 H	. . .	17	5·6	5·33 „ 5·54
Ba	. . .	68	22·5	22·16 „ 22·75
12 O	. . .	96	32·1	
$C_{20}H_{17}BaO_{12}$		301	100·0	

Anisoate of Silver, $C_{20}H_{17}AgO_{12}$.—Obtained by decomposing the baryta-salt with sulphate of silver, or by digesting the acid with carbonate of silver. Dissolves readily in water; also crystallises in nodular crystals, and while moist easily acquires a blackish tint.

		Calculated.		Found.
20 C	. . .	120	35·2	34·1
17 H	. . .	17	4·9	4·0
Ag	. . .	108	31·6	32·2
12 O	. . .	96	28·3	
$C_{20}H_{17}AgO_{12}$		341	100·0	

The difference between the experimental and calculated results must be attributed to the tendency to decomposition above noticed.

3. *Preparation of Aldehydes from the Acids* $C_nH_nO_4$.

It has long been known that when many salts of the acids $C_nH_nO_4$ are heated, they yield, simultaneously with the ketone of the series, a body isomeric with, and in many respects similar to, the aldehyde (propylal, butyral, and valeral); but aldehydes, such as are produced by oxidation of the alcohols, have not yet been obtained from the acids.

From the existing views of the constitution of the acids $C_nH_nO_4$, and of the ketones and aldehydes, as well as from the decomposition which takes place in the formation of the ketones, we may conclude that the aldehydes must be produced by an analogous process.

The formation of the ketone always requires 2 atoms of the salt.

$$\underset{\text{Acetate of lime.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\Ca\end{matrix}\right\}}O_2 + \underset{\text{Acetate of lime.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\Ca\end{matrix}\right\}}O_2 = C_2Ca_2O_6 + \underset{\text{Acetone.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\C_2H_3\end{matrix}\right\}}$$

Of 1 equivalent of the acetate of lime there remains only the radical, acetyl [othyl] or formyl-methyl, of the second only the methyl, which unite to form acetone, while the remaining elements form carbonate of lime.

When [as shown by Williamson*] a mixture of the salts of two different acids—*e. g.* valeriate and acetate of lime—is heated, the same metamorphosis takes place, 1 eq. of carbonate of lime being formed, and a ketone composed of the radical of the one acid, and the alcohol-radical contained in the other:

$$\underset{\text{Acetate of lime.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\Ca\end{matrix}\right\}}O_2 + \underset{\text{Valerate of lime.}}{\left.\begin{matrix}C_2(C_8H_9)O_2\\Ca\end{matrix}\right\}}O_2 = C_2CaO_6 + \left.\begin{matrix}C_2(C_2H_3)O_2\\C_8H_9\end{matrix}\right\}$$

$$\text{or } \left.\begin{matrix}C_2(C_8H_9)O_2\\C_2H_3\end{matrix}\right\}$$

If now formiate of lime be heated with the lime-salt of another acid of the series $C_nH_nO_4$, and the mixture subjected to distillation, a ketone is formed, containing an equivalent of hydrogen in place of the alcohol-radical: that is to say, an aldehyde.

$$\underset{\text{Acetate of lime.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\Ca\end{matrix}\right\}}O_2 + \underset{\text{Formiate of lime.}}{\left.\begin{matrix}C_2(H)O_2\\Ca\end{matrix}\right\}}O_2 = C_2CaO_6 + \underset{\text{Aldehyde.}}{\left.\begin{matrix}C_2(C_2H_3)O_2\\H\end{matrix}\right\}}$$

In this manner several aldehydes have been prepared by M. Ritter.

Acetaldehyde, $C_4H_4O_2$.—Dry formiate and acetate of lime, mixed in equivalent quantities, were heated in a retort over the open fire; the distillate being received in cooled ether and saturated with ammoniacal gas; crystals of aldehyde-ammonia then separated in considerable quantity. In this operation, especially when considerable quantities of material were used, a quantity of empyreumatic products was also formed, in consequence, partly of imperfect mixture, partly of too high a temperature being applied.

Propylaldehyde, $C_6H_6O_2$.—Propionate of baryta prepared from cyanide of ethyl was mixed with formiate of lime and distilled. Small quantities only were available for the experiment, and the distillate, amounting to only a few grammes, had therefore to be subjected to analysis after two rectifications, in each of which only the first portion was collected. The separation of the aldehyde by

* Chem. Soc. Qu. J. iv. 238.

combination with bisulphite of ammonia could not be effected, because the product was contaminated with propione. The boiling point of the propylic aldehyde used in the analysis lay between 48° and 55° (propylal obtained from butyracetate of lime boils at 66°). The analysis gave 58·03 per cent. C, and 10·31 H; the formula $C_6H_6O_2$ requiring 62·0 C, and 10·3 H. The numbers found by analysis would give for the ratio of the equivalents C : H : O = 6 : 6·2 : 2·5. As it was impossible to purify the product satisfactorily, the result may be considered as sufficient evidence that propylaldehyde was really formed.

Valeraldehyde, $C_{10}H_{10}O_2$.—Formiate and valerate of lime were distilled together; the portion of the distillate which boiled at about 100° treated with bisulphite of soda; and the resulting sulphite of valeraldehyde and sodium analysed. The analysis gave 31·71 per cent. sulphurous acid, the formula $C_{10}H_9NaS_2O_6 + 3$ eq. requiring 32·13 per cent.

Oenanthol, $C_{14}H_{14}O_4$.—By distilling a mixture of œnanthylate and formiate of lime, an oil was obtained, which combined with bisulphite of soda in crystalline laminæ having the appearance of sulphite of œnanthyl and sodium; the oil separated from these crystals by acids possessed the odour of œnanthol.

Caprylaldehyde, $C_{16}H_{16}O_2$.—The distillate obtained from caprylate and formiate of lime exhibited the odour of caprylic aldehyde, and formed a crystalline compound with bisulphite of soda.

Myristate and palmitate of lime distilled with formiate of lime yielded very offensive products, which were for the most part oily, and deposited only small quantities of solid substances. The latter, after pressure and repeated crystallisation from hot alcohol, consisted of small, perfectly white, inodorous crystalline scales, but yielded by combustion much larger quantities of carbon and hydrogen than is consistent with the composition of myristic and palmitic aldehyde. Probably these aldehydes cannot exist at the high temperature required to decompose the mixed salts.

The preparation of the aldehydes by this method will not, perhaps, be often advantageous; because empyreumatic products are formed at the same time in rather considerable quantity; and the presence of these products prevented the œnanthylic and caprylic aldehydes from being purified sufficiently for analysis; or the experiment should have been made on a much larger scale. Perhaps the occurrence of these impurities may be prevented by heating the saline mixture in an oil-bath, the temperature being maintained as little as possible above that which is required for the decomposition.

On Anisic Alcohol.*

By S. Cannizzaro and C. Bertagnini.

Cannizzaro† found that hydride of benzoyl, $C_{14}H_6O_2$, when treated with an alcoholic solution of potash, is converted into benzoic acid and the corresponding alcohol $C_{14}H_8O_2$. According to Cannizzaro and Bertagnini, hydride of anisyl, $C_{16}H_8O_4$, is in like manner converted into anisic acid, $C_{16}H_8O_6$, and a corresponding alcohol, $C_{16}H_{10}O_4$, viz. *anisic alcohol.*

To prepare the hydride of anisyl, anisol is gently boiled for an hour with about three times its volume of dilute nitric acid of 14° Baumé, after which the heavy oily product is washed with water, then with dilute potash-ley, and distilled. To separate the hydride of anisyl from the accompanying substances, the distillate is shaken up with a warm solution of bisulphite of soda of 30° Baumé; the resulting crystalline compound left to drain after cooling; washed with alcohol till it is perfectly white, and the alcohol which runs off no longer becomes turbid when mixed with water; the compound then dissolved in the smallest possible quantity of hot water, and heated with an excess of strong solution of carbonate of potash. The hydride of anisyl, which separates in the form of an oily layer rising to the surface, is then taken off and freed from any saline liquid that may be enclosed in it, by distillation.

When hydride of anisyl thus prepared is dissolved in an equal volume of alcohol, and this liquid mixed with three times its bulk of alcoholic potash-solution of about 7° Baumé, an action takes place attended with slight evolution of heat; and anisate of potash separates out in such quantity that the liquid solidifies to a crystalline pulp. After 10 or 12 hours, the alcohol is distilled off in the water-bath, the residue diffused in water, and the liquid heated with ether to extract the anisic alcohol, which, after the evaporation of the ether, remains in the form of a brown oil. On distilling this oil, a colourless liquid passes over at about 260° C, which, if the temperature of the air is low, soon crystallises: this product is anisalic alcohol. When thus prepared it generally retains a portion of unaltered hydride of anisyl, which may be easily recognised by its power of forming crystalline compounds with concentrated solutions of alkaline bisulphites. To remove this impurity, the preparation must be again treated with a small quantity of alcoholic potash-solution, then distilled in a stream of

* Il nuovo Cemènto, i. 99; Ann. Pharm. xcviii. 188.

† Chem. Soc. Qu. J. vii. 192.

carbonic acid, and the distillate, after solidifying, pressed between filtering-paper.

Pure anisic alcohol thus prepared distils without decomposition at 248° to 250° C; melts at about 23° when anbydrous, but at a lower temperature (as low as 7°) when moist. Crystallises in hard shining needles.

		Calculated.	Found.			
16 C	96	69·56	69·21	69·51	69·32	69·60
10 H	10	7·24	7·33	7·30	7·37	7·30
4 O	32	23·20	23·46	23·19	23·31	23·10
$C_{16}H_{10}O_4$	138	100·00	100·00	100·00	100·00	100·00

Anisic alcohol is heavier than water; has a faint spirituous and sweetish odour, and a burning taste resembling that of oil of aniseed. It does not alter by exposure to the air at ordinary temperatures, even for a long time; but when heated nearly to its boiling point, it absorbs oxygen, and is converted into hydride of anisyl.

Oxidising substances convert anisic alcohol, with the greatest ease, first into hydride of anisyl, then into anisic acid. In contact with platinum-black, it emits, after some time, the odour of hydride of anisyl, and after a few days the entire quantity of the anisic alcohol is converted into anisic acid. Dilute nitric acid, with the aid of heat, likewise brings about these changes in succession.

Anisalic alcohol heated with various salts, *e. g.* benzoate, anisate, and acetate of potash, dissolves them, but deposits them again on cooling. It likewise dissolves several organic substances, *e. g.* salicia, phillyrin, and hippuric acid.

Potassium introduced into liquid anisic alcohol causes an evolution of hydrogen, which becomes very violent on the application of heat. The resulting potassium-compound remains dissolved in the yellow liquid while warm, but the whole solidifies into a buttery mass on cooling.

Sulphuric acid, even when but moderately concentrated, converts anisic alcohol into a reddish resinous mass. Anhydrous phosphoric acid exerts a similar action. When the alcohol is moderately heated with chloride of zinc, a violent action takes place; water is formed, which unites with the chloride of zinc, and an oily liquid rises to the surface, which on cooling solidifies in a hard transparent, vitreous mass, melting at 100°, insoluble in water and alcohol, but soluble in sulphide of carbon.

Chlorine gas passed into anisic alcohol is absorbed, with evolution of heat, the liquid becoming turbid, and ultimately sepa-

rating into two layers, the lower of which is aqueous hydrochloric acid, while the upper appears to be the chlorine-compound of the radical contained in the alcohol. This upper liquid, when quickly washed with a dilute solution of carbonate of potash, and then with water, forms a colourless oil, having a fruity odour and burning taste. In contact with an alcoholic solution of ammonia, it is quickly decomposed, with formation of sal-ammoniac and a liquid which exhibits all the properties of anisic alcohol. This substance appears also to undergo a similar decomposition in contact with solutions of alkaline carbonates. It was not obtained in sufficient quantity for analysis. Want of material likewise prevented the formation of other compound ethers from anisic alcohol. In an attempt to prepare anisic ether by the action of chloride of anisyl on the alcohol, a violent action was observed, attended with abundant evolution of hydrochloric acid vapours, and formation of anisic acid, and a resinous substance insoluble in alcohol and ether, but soluble in chloroform.

Hydride of salicyl (salicylous acid), $C_{14}H_6O_4$, treated with potash in aqueous or alcoholic solution, either at high or at low temperatures, combines with the alkali, without undergoing further alteration when heated; it is only when the potash-hydrate has become solid by evaporation, and then melts at the higher temperature, that the salicylate of potash formed at the beginning of the action is converted, as is well known, into salicylate. This process, therefore, does not yield the alcohol corresponding to salicylic acid. The composition proper to this alcohol is exhibited by saligenin, which likewise behaves like an alcohol in certain points (conversion into an aldehyde, the hydride of salicyl by certain oxidising agents; and conversion into salicylate of potash, with evolution of hydrogen, when heated with hydrate of potash), but neither possesses the volatility of other alcohols, nor forms ethereal compounds with acids.

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XI.—*On Cadmium-ethyl.*

By J. A. Wanklyn,

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The close analogy subsisting between zinc and cadmium led me to expect that the latter would form a compound with ethyl corresponding to zinc-ethyl. In consequence of this expectation I instituted a preliminary experiment, which satisfied me that such is really the case. I then referred to the journals,* and saw that already, in 1853, Schüler had made an investigation with a similar object in view, but that he had altogether failed in the attempt. In the account which he has published of his experiment one or two little omissions struck me, which omissions, I believe, caused him to arrive at no positive result.

These considerations at once determined me to pursue the subject, and accordingly I made a number of preliminary experiments on the action of cadmium on iodide of ethyl mixed with ether. Several times in the course of these experiments I obtained undoubted proof of the existence of a body containing cadmium in combination with organic matter, and volatile below 200° C. In order to procure a sufficient quantity of the new substance for an examination of its properties, I resolved on performing an experiment on a large scale, which experiment I now describe at length.

* Ann. Ch. Pharm., lxxxvii., 56, 57.

About 2,000 grains of cadmium was beaten out into a thin lamina, which was then cut up by means of scissors into very narrow strips. Thus prepared, the metal was introduced into the copper digester used in the manufacture of zinc-ethyl. Perfectly dried iodide of ethyl and ether, 1,000 grains of the former and about an equal bulk of the latter, were next poured in. Then the digester was closed air-tight, and heated up to 130° C. for about an hour. The temperature was next lowered to 100° C. and not suffered to rise above that point during the remainder of the digestion. The whole time occupied by the digestion was about 50 hours, but this process was not continued uninterruptedly throughout that period, as the operation was arrested at night. Having completed this part of the process, the digester was allowed to cool, and afterwards opened by removing the screw-plug. Immediately a considerable quantity of gas escaped. A bent tube was then adapted, and the distillation made in an atmosphere of dry carbonic acid, just as recommended by Frankland in his memoir on zinc-ethyl. The disposition of the apparatus, and the general mode of performing this experiment, were such as Frankland has detailed in his memoir on zinc-ethyl, and to that paper I refer.*

During this distillation, a large quantity of ether and iodide of ethyl came over, but no fumes were evolved at temperatures below 170° C. When the temperature had reached 160° C. the receiver was changed, and between 180° C. and 220° C. a colourless fuming liquid distilled. This liquid, when exposed to the air, evolved first white fumes, and then brown fumes, owing to the formation of oxide of cadmium, and finally burst into flame, depositing brown spots on neighbouring objects. It effervesced with water, forming at the same time a white precipitate. In this respect it resembles zinc-ethyl, as also by the formation of a white solid on the slow absorption of oxygen. Its smell was peculiar, and not disagreeable, rather like that of zinc-ethyl. An estimation of cadmium was made by treatment with water. The precipitate so obtained was dissolved in dilute nitric acid, and the resulting solution evaporated to dryness, and finally ignited, when it left a residue of the deep brown colour characteristic of oxide of cadmium.

Treated in this way, 0·2085 grammes of the liquid gave 0·0877 grammes of oxide of cadmium. As a test of the purity

* Transactions of the Royal Society, 1855, p. 259.

of the oxide of cadmium, it was converted into chloride of cadmium, and weighed in that form, with these results:

Calculated.	Found.
0·0877 CdO	0·0877 CdO
0·1250 CdCl	0·1255 CdCl

The foregoing analysis proves that the distillate contained 36·78 per cent. of cadmium, which indicates that the substance was impure. This circumstance was by no means unexpected, as the total amount of distillate which came over above 160° C. did not much exceed one gramme and a half, and so small a quantity would be rendered very impure by the residual vapour of ether in the digester. If we take the formula of the new substance to be Cd C_4 H_5, the distillate would contain 55·92 per cent. of this substance. The remainder of the percentage would be ether, iodide of ethyl, and perhaps hydrocarbons—the result of the decomposition of this cadmium-ethyl whilst it was in the digester.

In order to obtain the new substance pure, the obvious course was to redistil the crude product, and endeavour to obtain a constant boiling point. For that purpose, more crude cadmium-ethyl was requisite. As the action in the digester had been very far from complete, the ether and iodide of ethyl which had come over first were poured back, along with a further quantity of these ingredients, into the digester, which was closed and heated to 125° C. for two or three days.

On submitting the product to distillation, the ether which came over below 170° C. was collected apart, and the receiver changed after the white fumes had been observed for some time. This second part of the distillate, which fumed as in the former operation, was redistilled in the oil-bath, but no constant boiling point could be obtained. The liquid boiled or evolved gas rapidly up to 165° C., indicated by a thermometer placed in the vapour, and deposited metallic cadmium on the sides of the flask, although the temperature of the surrounding oil-bath was never higher than 210° C. What came over between 95° C. and 165° C. was collected apart, and was found to be greatly altered in properties and composition. On exposure to the air, it fumed a little, but would not inflame spontaneously. Subjected to analysis it gave the following results: 0·093 grms. on treatment with nitric acid and subsequent ignition, yielded 0·0118 grms. of residue. In a second experiment 0·3228 grms. of substance gave, when similarly treated, 0·0387 grms. of residue. These residues, unlike that pre-

viously mentioned, contained, in addition to the oxide of cadmium, a quantity of oxide of zinc, and, instead of being brown, were white.* A combustion with oxide of copper was also made, wherein 0·1852 grms. of substance gave 0·4218 grms. of carbonic acid, and 0·1962 grms. of water.

Here are the collected per centage results of these analyses:

	I.	II.	III.
CdO and ZnO	12·69	11·99	
C			62·11
H			11·77

These numbers show that distillation decomposes in great part the ethyl-compound of cadmium.

The changes which ensue during the action of the materials in the digester present some points of interest, and were made the subject of study. Perfectly dry cadmium, ether, and iodide of ethyl, were sealed up in a glass tube, which was then placed in the water-bath, and frequently agitated during the digestion. For the first five hours there was no visible action. During the next ten hours some crystalline powder was deposited, afterwards the action seemed very rapid; the cadmium underwent great diminution in volume, and a large quantity of shining powder occupied the tube. This powder appeared more soluble in the liquid within the tube whilst hot than when cold. On breaking the tube and bringing out the contents into the air, they did not fume at all; very unlike the behaviour of the resulting oily body which exists in the digester previously to the distillation of zinc-ethyl. Yet this powdery substance, which did not fume, became hot on exposure to the air, and effervesced violently with water, giving a precipitate soluble in acids. In the distillation of cadmium-ethyl, as I have many times noticed, no fumes are given off until a temperature of about 170° C. has been attained; whilst with zinc-ethyl, hardly any of the ether distils before the fuming on exposure to air commences. These facts go to prove that, as first formed, and previously to distillation at 170° C., the cadmium-ethyl exists in stable combination with iodide of cadmium. In the case of zinc, there is a feeble compound of iodide of zinc with zinc-ethyl, as was pointed out by Frankland.† But a tempera-

* The appearance of zinc in this situation rather surprised me, as the cadmium employed in the experiments was almost absolutely free from zinc. Furthermore, I made an experiment some time ago on the behaviour of brass filings on iodide of ethyl at 150° C. I found that there was no action.

† Transactions of the Royal Society, 1855, p. 263.

ture which almost utterly breaks up the zinc compound into zinc-ethyl and iodide of zinc, fails to resolve the corresponding cadmium body into its proximate constituents. Some attempts were made to obtain this double compound of cadmium-ethyl with iodide of cadmium in a state of purity, but without success, as no means of separating the free iodide of cadmium from the double compound presented themselves. Ether dissolves iodide of cadmium slightly, especially under pressure, and ether appears to behave similarly with the double compound.

The contents of the digester, after the cadmium-ethyl had been distilled off in the experiment on the large scale, were examined. They consisted of cadmium unchanged and a grey powder. This residue was treated with hot water, and filtered. The filtrate was evaporated to dryness, and the solid product powdered and dried at a temperature considerably above 100° C. It proved to be pure iodide of cadmium, and gave the following results on analysis:

	Calculated.		Found.
I . .	126·88	69·48	69·42
Cd . .	55·74	30·52	30·29
	182·62	100·00	99·71

The residue on the filter from which the iodide of cadmium had been washed out contained some oxyiodide of cadmium, which, in all probability, was an after product, due to the reaction of finely-divided metallic cadmium on iodide of cadmium when exposed to air and moisture. This insoluble grey powder, which has obviously its origin in the decomposition of cadmium-ethyl previously formed, was very considerable in quantity; a fact which proves that a considerable amount of cadmium-ethyl had been in existence at some period of the operation.

In the experiments on the large scale, about 100 grammes of iodide of ethyl had been employed in the two operations, yet the entire amount of cadmium-ethyl which distilled over in these operations could not exceed 3 grammes. It follows, therefore, that a large proportion of cadmium-ethyl had been decomposed.

Seeing that the contents of a tube—in which cadmium has been digested with iodide of ethyl and ether in the water bath—are a white shining powder previously to distillation, and seeing that products examined subsequently to distillation consist of a

grey powder, I am entitled to conclude that this decomposition of the cadmium-ethyl goes on to a great extent during distillation.

I have arrived at the conclusion that the temperature required to decompose the double compound of iodide of cadmium and cadmium-ethyl breaks up nearly all of the cadmium-ethyl, a small proportion only of that substance being carried over unchanged by the hydrocarbons generated in that decomposition.

As cadmium-ethyl will not distil at ordinary pressures without undergoing decomposition, it was suggested to me by Professor Frankland that cadmium-methyl would be a more favourable body for investigation than the subject of this memoir; and as the presence of iodide of cadmium is a troublesome complication, it was likewise suggested that an alloy of sodium and cadmium should replace cadmium in the proposed experiments.

It has occurred to me also that the employment of an alloy of cadmium and zinc cannot fail to yield interesting results, which may throw great light upon the mode of formation and composition of this class of bodies. This last-mentioned train of research is already in progress, and that named immediately before will be begun as soon as practicable.

No one who reads this paper will doubt that the discovery of zinc-ethyl was an indispensable preliminary to that of cadmium-ethyl. To Professor Frankland for that, and assistance of a more personal nature, I return thanks.

XII.—*On a Coal-Gas Carbon and Nitric Acid Voltaic Battery.*

By James L., and L. Wheeler.

It will be readily acknowledged that Grove's nitric acid and platinum battery is hitherto unequalled for the quantity and tension of the electricity evolved. It may, therefore, be regarded as the instrument of standard excellence. The great expense of the platinum, is, however, an obstacle to its general introduction. Many years ago, the late Mr. John Thomas Cooper first suggested the use of carbon in the construction of the voltaic apparatus, and Professor Bunsen is known to have followed in the same

track. Bunsen's battery is made with a great amount of trouble; and, when constructed, is liable to objections, particularly that, after some use, it becomes inefficient from the porosity of the carbon, which causes the rapid corrosion of the metallic connexions.

Ordinary graphite is a form of carbon, remarkable for its high power of conducting electricity, and we made many experiments for applying it as the receiving surface in the nitric acid battery. The difficulties of this application soon showed themselves to be insuperable. In the first place, small plates only of this substance are obtainable, many of which were entirely disintegrated as soon as they were brought into contact with nitric acid: its brittleness also is such as to render it unmanageable. Having abandoned the common graphite battery, our attention was next turned to a modification of Daniell's, by bringing the zinc and copper plates much closer together than in his original form of apparatus. The quantity of sulphate of copper, dissolved by dilute sulphuric acid, is soon decomposed by the hydrogen eliminated from the zinc plate, hence the necessity of a constant supply of the salt to keep up the saturation of the acid. In one experiment with two pairs of Daniell's cells, excited by dilute sulphuric acid, saturated with sulphate of copper, there was only a slight spark between points of carbon, and hardly any perceptible decomposition of water. The copper plates used in this instance measured $5\frac{1}{2}$ inches by 3, and were surrounded in an outer cell by a double zinc plate, well amalgamated. No amount of platinum wire could be ignited by this arrangement. To maintain a large supply of oxide of copper in solution, recourse was had to the nitrate, a salt so much more soluble than the sulphate. In this instance, a very manifest increase of power was obtained, as an inch of fine iron wire was ignited by two pairs of cells, while with the sulphate no such effect was produced. A saturated aqueous solution of the nitrate was employed.

Our attention was next directed to the application of the carbon deposited in the interior of coal-gas retorts, as the receiving surface in a cell with nitric acid, this carbon being liable to no disintegration from contact with acids.

Difficulties were at first apprehended in procuring plates of sufficient size. We found, however, that it could be readily sawn across in the thinnest direction, by the aid of a piece of cast iron and sharp sand; the plate could then be finished by grinding it with sand upon a stone. As entire plates of the coal-gas carbon

could thus be obtained, we introduced two of them into cells with nitric acid. The shape of these plates was slightly irregular, their dimensions being nearly 5½ inches by 3. Five inches of platinum wire, of the 50th of an inch diameter, were heated to dull redness, and, from the mean of three experiments, 1·9 cubic inch of the gases, from the decomposition of water, were collected in 4 minutes 43 seconds, a strong solution of carbonate of potash being employed with iron electrodes.

These two pairs of plates were compared with two pairs of Grove's, with platinum plates of the same dimensions as those of the carbon. The two pairs of Grove's plates evolved from the same solution 1·9 cubic inch of gases in 4 minutes 45 seconds, or 2 seconds more than with the carbon plates. The same length of the same platinum wire was ignited in each case. In these two experiments the greatest care was employed in inserting as many pieces as possible of amalgamated zinc plate between the generating plate and porous cell, by which means the internal resistance to the current was reduced to a minimum. The plates of gas carbon were connected by slips of platinum foil, supported above by slips of sheet zinc, which served to give them strength, and increase their conducting power by keeping them cool. The dilute sulphuric consisted of five measures of water and one of acid. The nitric acid was the ordinary material of commerce.

On one occasion, the immersion of the plates in the acids was continued for six hours without any material diminution of power.

XIII.—*Description of a Self-acting Washing Bottle.*

By William Stephens Clark,

student of chemistry in the laboratory of st. thomas's hospital.

In the "Philosophical Magazine" for August, 1849, a simple apparatus for washing precipitates is described by Mr. Summers, which acts by an adaptation of two concentric tubes to the lower extremity of a washing bottle.

The following apparatus is founded on the same principle; but

the concentric tubes, being passed through a cork at the top of the reservoir, the instrument is perhaps more convenient for general use.

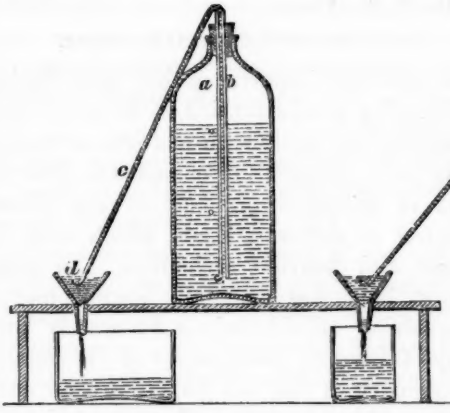

Fig. 1.

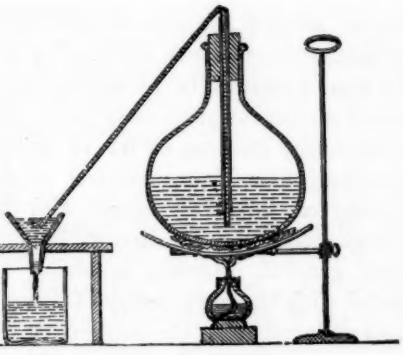

Fig. 2.

A wide tube (*b*) is inserted in the cork of a bottle (*a*), so as nearly to touch the bottom. A narrow tube (*c*) is bent into the form of a syphon, the shortest limb of which is a little longer than the wide tube, and the other of such a length that when the short one is perpendicular, the two ends of the tube will be on the same level. The end of the longer limb (*d*) is slightly recurved, in order that the water may not disturb the precipitate.

The bottle is now filled with water, the cork fitted tightly in, and it is placed so that the bottom of the wide tube may be below the edge of the filter paper in the funnel. The narrow tube is placed inside the wide one as in the drawing; then by blowing down the wide tube, water is forced up through the syphon into the funnel, but will not be able to rise above the level of the bottom of the wide tube, and consequently cannot reach the top of the filter paper.

If, instead of a bottle, a thin glass receiver is used (Fig. II.), heat may be applied, and the water in the funnel will be kept warm; but care must be taken not to allow the water to boil, as in that case the water would be forced too fast through the syphon, and might overflow the wide tube, and crack the receiver.

XIV.—*On the Composition of some Varieties of Foreign Iron.*

By F. A. Abel,

DIRECTOR OF THE CHEMICAL ESTABLISHMENT OF THE WAR DEPARTMENT.

There are few subjects of practical importance that have, during the last twelve months, attracted general attention in this country to the same extent as the question of the manufacture of iron ordnance. While numerous plans have been proposed, discussed, and tried for constructing cannon, either of wrought-iron, steel, or mechanical combinations of iron-material of different kinds, which shall be capable of throwing larger and heavier projectiles than those hitherto used, the question at issue has gradually become one of more general interest, involving considerations intimately connected with the metallurgy of iron, in consequence of the conclusions deduced from the experience in the late war, that the conditions necessary for obtaining a durable and uniform material for iron guns are as yet far from being fully determined.

The American Government has lately published a collection of reports, containing some interesting and important observations connected with the manufacture of iron ordnance, though it does not appear that the researches carried on in that country, or the experience gained by the directors of gun foundries belonging to various continental states, have as yet effected much more than the provision of a number of data relating to the nature and quality of iron employed, the different methods of treating the metal and of casting the gun, and the effects of mechanical tests and of the explosive force of powder upon iron ordnance. There is little doubt that the accumulation of such data, and extensive experiments suggested by their comparison, will ultimately lead to the establishment of the conditions necessary for insuring to iron ordnance uniformity and durability.

The collection in this country of such data as those referred to has hitherto been a matter of great difficulty, from the circumstances that iron ordnance were obtained by Government from various private sources; that no special conditions have been observed in the selection or treatment of metal for ordnance; that no records of the material employed by the different manufacturers have been preserved, and that no system of tests, physical or chemical, has been applied to the metal composing the guns, beyond the regulation proof to which ordnance were submitted before their acceptance from manufacturers. It is obvious also, from these

circumstances, that no uniformity in the iron guns used in this country could be expected.

Now that Government has determined to take the manufacture of iron ordnance into its own hands, the most serious obstacles to the perfection of these important arms in England are set aside, and the introduction of a complete system of testing and of record, together with the results of a very extensive series of experiments, on a sufficient scale, which have already been commenced, will, it is hoped, furnish important contributions to our knowledge of the constitution and mode of treatment of iron, best adapted for the manufacture of ordnance.

In carrying out the system of experiment determined upon by Government, attention has been directed, in the first place, to iron reduced from its ores by charcoal, this being the material employed exclusively, in some continental States, and to a very great extent in others, in the manufacture of iron ordnance. Much stress is laid, by many authorities on the continent, upon the greater fitness, for this purpose, of that description of iron than of the best hot-blast, or even of cold-blast iron, smelted with coal or coke. It appeared, therefore, naturally the first step, in comparative experiments with various materials, to ascertain the nature of the iron composing the most durable guns manufactured in those countries, and to determine, by comparative experiments here, whether guns manufactured from charcoal-iron exhibit great superiority over those made *according to the same system* of iron reduced from its ores by mineral fuel. Various specimens of foreign charcoal-pig-iron, and cannon of that metal made in France, Belgium, and Sweden, have been collected for comparative examination, and considerable quantities of charcoal-iron, procured from Nova Scotia, Sweden, and America, have been purchased, for experimental purposes. The results obtained, up to the present time, are principally those furnished by the analysis of several of these specimens; and I venture to submit these to the Chemical Society, as they exhibit some points of interest, and may also serve, to others engaged in similar inquiries, as additional means, to those already existing, of comparing the constitution of the varieties of charcoal-iron with that of other descriptions of iron.

It is unnecessary, in the present instance, to enter into analytical details; but, as various methods are employed, by different chemists, for determining the most important constituents in iron, it may be advisable to furnish a brief outline of those adopted in performing the subjoined analyses.

The *graphite* was determined by digesting the finely-pulverized iron with concentrated hydrochloric acid, and boiling the residue for some time with a moderately-strong solution of potassa: the graphite was collected, washed, dried, and weighed. It was afterwards placed in a capsule and heated to redness in a muffle, until the whole of the carbon was burnt off. The weight of the slight incombustible residue which was generally obtained was deducted from the weight of the graphite.

For the determination of the *total amount of carbon* the iron was reduced to an extremely fine state of division; it was then first mixed with about twice its bulk of fine sand, or powdered glass, and afterwards with a mixture of chromate of lead and chlorate of potassa. The combustion was conducted in the usual manner, a current of oxygen being frequently employed.

The proportion of *silicium* was ascertained by acting upon the finely-divided metal with concentrated hydrochloric acid, evaporating to dryness, and digesting the residue with hydrochloric acid. The insoluble portion was collected upon a filter, washed until free from iron, dried, and ignited until the whole of the carbon was burnt off. The silicic acid thus obtained was digested with solution of potassa, after its weight had been determined. If any insoluble residue was obtained its weight was deducted from that of the silicic acid.

To determine the proportion of *sulphur*, hydrochloric acid was allowed to act very slowly upon fragments of the iron, in a suitable apparatus, and the gas generated was passed through a slightly acid solution of acetate of lead. The sulphide of lead produced was collected, washed, and ultimately weighed as sulphate of lead.

The *phosphorus* was determined by digesting, in nitrohydrochloric acid, fragments of the metal, of the size of small peas, evaporating the solution to dryness, digesting the residue with hydrochloric acid, and separating the insoluble from the soluble portion. The hydrochloric solution was partly neutralised by sesquicarbonate of ammonia, and the greater part, if not the whole, of the sesquichloride of iron reduced to protochloride, by sulphite of ammonia. Solution of acetate of ammonia was then added in excess, and afterwards a small quantity of solution of sesquichloride of iron. The phosphate of iron was precipitated by boiling, collected, and dissolved in hydrochloric acid, and decomposed by sulphide of ammonium. The phosphoric acid was estimated in the usual manner, as pyrophosphate of magnesia.

In the following table is represented the percentage composition

of several specimens of iron, reduced from its ores by charcoal, as calculated from the analytical results:—

TABLE I.

Composition of Pig Iron smelted with Charcoal obtained from

	Nova Scotia.			America.			France.	Silesia.	
	Grey.	Mottled.	White.	Grey.	Mottled.	White.	Grey.	White, *very crystalline.*	White, *less crystalline.*
Specific gravity...	7·120	7·540	7·690	7·159	7·540	7·675	7·000	7·531	7·604
Iron.....	95·20	95·35	95·25	94·87	96·35	96·55	95·18	93·45	90·75
Combined Carbon	—	1·72	2·96	·04	1·14	2·79	—	4·94	3·62
Graphite.....	3·11	1·38	—	3·07	1·50	—	3·40	—	—
Silicium	1·11	·26	·21	1·80	·79	·32	·80	·75	·25
Sulphur	·01	·03	·02	trace	·01	·06	·03	trace	trace
Phosphorus	·13	1·30	1·53	·22	·20	·17	·45	·12	3·26
Manganese	·25	trace	—	trace	trace	trace	—	5·38	2·00
Copper	—	—	—	trace	trace	trace	—	·24	trace
	Traces of Titanium and Cobalt.						Traces of Arsenic and Chromium	Traces of Cobalt.	

The specimens of white iron from Silesia differ from one another in several respects, and to such an extent, as to prove that they were obtained from different ores. Both were very hard and brittle; but the ore containing the largest amount of manganese exhibited a foliated structure and brilliancy of lustre, very similar to that of refined antimony, while the other specimen, rich in phosphorus, was less brilliant and far more compact. These irons were proposed for admixture with dark grey iron; but it was considered that they could not be advantageously employed for this purpose.

The French iron examined was a specimen of the metal reduced by charcoal from hæmatite-ores, at the Government cannon foundry of Ruelle, and employed exclusively in admixture with charcoal-iron also reduced from similar ores in the neighbourhood, for the manufacture of ordnance. It was dark, soft, fine-grained, and uniform in texture. In its general characters it was similar to

the Swedish grey iron analysed, though exhibiting a superiority over the latter in reference to the amount of silicium it contains.

The specimens of American and Nova Scotia iron analyzed were taken as average samples from large parcels of the metal purchased by Government for experimental purposes.

The different varieties of iron from each source exhibit such differences in their composition as are generally observed in irons reduced from the same ore under modified conditions. Both the Nova Scotia and American irons are of excellent quality, and furnish the best results when submitted to physical tests. Comparative trials are about to be made of their merits as gun-metal.

The subjoined table exhibits the results of the analyses of four specimens, from guns of foreign manufacture.

TABLE II.

Composition of Iron Gun Metal from

	Belgium.	France.	Sweden.	Russia.
Specific gravity	7·250	7·250	7·050	7·135
Iron	95·61	96·02	95·87	94·36
Combined Carbon	·78	1·03	·18	·47
Graphite	2·12	1·87	2·62	2·83
Silicium	·99	·35	1·19	1·10
Sulphur	·06	·03	·08	·02
Phosphorus	·29	·45	·11	·37
Manganese	·15	·25	trace	·85
Titanium	traces	traces	trace	trace
	Traces of Chromium, Arsenic, Zinc, and Copper.	Traces of Chromium and Tin.	Traces of Chromium.	Traces of Tin.

The Swedish metal examined has great resemblance to that composing the Russian gun which was one of those lately captured and selected for experiment. A severe proof to which this gun was submitted showed that the metal composing it was of excellent quality.

The Swedish metal was of a uniform light grey colour, while the Russian gun exhibited a slightly mottled appearance. Both contained the graphite in a finely divided state. It is worthy of remark, that the strength and durability of Swedish iron guns is found to be variable; which circumstance is ascribed to the very

general practice of casting the guns directly from the blast furnace, instead of first submitting the metal to treatment in reverberatory furnaces.

The specimen of French gun-metal was obtained from the cannon foundry at Ruelle. It resembled, in a remarkable manner, several specimens of iron gun-metal obtained from the cannon foundry at Liège, of which the composition of an average sample is also given in the above table. Both kinds were mottled iron of very uniform character, exhibiting a short and regular fracture, and a fine and compact structure. Their specific gravities are identical, and the differences exhibited in their composition are but slight. For the preparation of the French gun-metal, a mixture of various descriptions of charcoal pig-iron, obtained at Ruelle, is made with grey pig-iron, from other similar iron works in the neighbourhood (*e.g.* from *La Chapelle* and *Etouars*) with old French cannon, and with the "dead-heads" from former castings. By a protracted treatment in reverberatory furnaces, these metals undergo thorough mixture, and purification at the same time, and are converted into the uniform mottled metal above referred to. The fuel used for the remelting and mixing is Newcastle coal.

At the Belgian Government cannon foundry a certain proportion of hot-blast iron, smelted with coke, is employed in admixture with old cannon, "dead heads," and charcoal pig-iron, obtained from various smelting works, more particularly in the neighbourhood of Charleroi. The fuel used for the remelting is a semi-anthracite coal, from Belle Vue, in the neighbourhood of Liège, and has the following percentage composition :—

Carbon	85·56
Hydrogen	4·20
Oxygen	2·40
Nitrogen	1·92
Sulphur	1·00
Ash	4·92

The percentage of phosphoric acid in the ash is 1·60.

The same care is taken to ensure the production of a metal of uniform structure, as at Ruelle; and the excellent results obtained by the proof of the guns, and by the mechanical tests to which the metal is submitted, bear very strong evidence in favour of the superiority of iron of the particular constitution and structure produced in Belgium and France, for the manufacture of guns, over other kinds of iron, even equal to it in chemical quality.

Unquestionably the repeated exposure of grey iron to a moderately oxidising action, in the reverberatory furnace, has the effect of improving its quality, and of removing one of the impurities most objectionable in iron which is to possess tenacity and elasticity, namely, silicium. In experiments lately made, in connection with some patent processes for improving the quality of iron, it was found that the oxidising action of air upon highly-heated iron had the effect of removing the silicium entirely, before the amount of carbon existing in the metal was diminished in any sensible degree. The close-grained and very uniform structure of the iron produced by the mixing and remelting processes, on the continent, and the very finely divided condition in which the graphite exists in the iron, are elements affecting the durability of the gun-metal, of equal importance to the purity of iron. Some pieces of iron ordnance which have either burst upon proof, or after having been but a short time in use, and the metal composing which was of good quality and even of an unusually pure description, evidently owed their incapability to resist the force of gunpowder to the comparatively loose structure of the metal, and to the existence of the graphite in large scales. There are, moreover, various points to be taken into consideration, in connection with the *method of casting guns*, which cannot be entered into here; but which, doubtless, greatly influence their physical structure and, consequently, their durability.

It would be premature to attempt a comparison between the merits of charcoal-iron and those of the better qualities of British cold-blast iron, as materials for ordnance, from results of analysis alone; but thus much is certain, that iron smelted with mineral fuel may be obtained in abundance in this country, which contains not more phosphorus or sulphur than are found in average specimens of charcoal-iron, and that abundant proofs already exist of the ease with which silicium may be removed from pig-iron, by judicious treatment. It may, therefore, be confidently expected that future experiments on the casting of ordnance, with various kinds of iron, will prove that we are not dependent upon a supply of charcoal-iron, for the production of durable guns.

As an appendix to this communication, I beg to lay before the Society the results of analysis of a specimen of the cast steel manufactured by Krupp, of Essen, of which such beautiful specimens were exhibited at the Paris Exposition of 1855.

This cast-steel was proposed, by M. Krupp, as a material for ordnance, as far back as 1847, and the first small gun (a 3 pr.)

cast of it was submitted to very severe tests, in Berlin, in 1849, and finally proved to bursting. A 12-pr. gun, of the same material, was afterwards sent for trial to this country (early in 1855), after having likewise withstood very severe tests. At about the same time, a cylinder of the cast steel was sent from Essen, and bored by Messrs. Walker, of the Gospel Oak Works, to the calibre of an 8-inch gun. Its breech was fitted with a cast-iron case, or jacket, the thickness of which was 10 inches at the breech, and 8·5 in front of the trunnions. The weight of the gun complete was 8 tons 5 cwt. The case was in contact with the steel barrel only at its two extremities, at the breech and the middle of the barrel; at the latter place a wrought-iron wedge-ring was fitted into the barrel, and fixed to the jacket by screws. This gun was proved at Woolwich, but burst the first time it was fired. The probable cause of this unexpected result has been a subject of some public discussion in Germany, but there is little doubt that it was due to the injudicious form of projectile (weighing 259 lbs.) which the parties who proposed to Government the experiments with cast steel, and provided the gun for trial, insisted upon employing for the proof.

The gun was broken into ten large pieces and a number of small fragments. The various fractures of the cast steel did not exhibit any imperfections, to which the bursting of the gun could have been ascribed. The metal was very uniform, compact, and hard. A fragment was selected for analysis, and furnished the following results:—

One hundred parts contained—

Iron	98·05
Combined carbon . .	1·18
Silicium	0·33
Phosphorus . . .	0·02
Manganese . . .	*trace*
Cobalt and Nickel . .	0·12
Copper	0·30

No sulphur was detected.

The specific gravity of the specimen analysed was found to be 7·836.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

BY HENRY WATTS, B.A., F.C.S.

On Insolinic Acid.*

By A. W. Hofmann.

On attempting to purify crude cuminic acid, by boiling it with a mixture of sulphuric acid and bichromate of potassium, it was observed that the cuminic acid is gradually transformed into a new acid, for which I would propose the provisional name of *insolinic acid.*

If one part of cuminic acid be boiled with 8 parts of concentrated sulphuric acid and 12 parts of water, care being taken to condense that which is volatilized, (viz., cuminic acid and water,) and to return it to the seat of the reaction by means of a long upright tube, connected with the flask, the transformation is accomplished in about 12 hours. The crystals of cuminic acid deposited in the neck of the flask and in the condenser-tube at the commencement of the operation disappear; and, after cooling, there will be found floating upon the green liquid a white flour-like powder (insolinic acid). This liquid also retains in suspension a greenish, half-fused mass (insolinate of chromium). The liquid is now filtered, the insoluble mixture washed with water, in order to remove the soluble chromium-salt, and the residue boiled with ammonia; insoluble sesquioxide of chromium is then separated, insolinic acid passing into solution. The ammoniacal solution, on saturation with hydrochloric acid, furnishes a white powder, which, when repeatedly boiled with water, or heated with boiling alcohol (for the purpose of removing any adhering cuminic acid), constitutes pure insolinic acid.

This substance is a white powder, tasteless and inodorous, and apparently without crystalline structure; it appears crystalline, however, under the microscope. Insolinic acid is scarcely dissolved by water; it is almost insoluble in alcohol, and perfectly insoluble in ether. From an aqueous solution, saturated when hot (which possesses a distinctly acid reaction), it is deposited on cooling in

* Ann. Ch. Pharm. xcvii., 197.

the form of a powder, consisting of extremely minute crystals. Insolinic acid is readily dissolved by the fixed alkalies, and also by ammonia, which it perfectly neutralizes. When boiled with the alkaline carbonates, it expels their carbonic acid. It is insoluble in concentrated sulphuric acid, and the solution may be heated without becoming black; on addition of water, the acid is reprecipitated unchanged; no effect results from continued ebullition with the strongest acid. Insolinic acid fuses only at a very high temperature; its fusing point and boiling point nearly coincide. Submitted to distillation, a portion of the acid sublimes unaltered, another portion is decomposed with formation of benzoic acid and benzol, carbonic acid being evolved, and a residue of carbon remaining in the retort.

Combustion of insolinic acid has furnished the following results:

I.	0·233 grm.	of acid	0·511	carbonic acid	0·087 water
II.	0·3325	„	0·724	„	0·130
III.	0·3005	„	0·6605	„	0·120

These numbers lead to the formula

$$C_9H_4O_4, \text{ or } C_{18}H_8O_8$$

	Theory.		Experiment.			
			I.	II.	III.	Mean.
C_{18} =	108	60·00	59·82	59·37	59·92	59·70
H_8 =	8	4·44	4.14	4·34	4·43	4·30
O_8 =	64	35·56	—	—	—	—
	180	100·00				

Hence follows that the new acid is derived from cuminic acid by the partial oxidation of its carbon and hydrogen, oxygen being fixed at the same time.

$$\underbrace{C_{20}H_{12}O_4}_{\text{Cuminic acid.}} + 12O = 2CO_2 + 4HO + \underbrace{C_{18}H_8O_8}_{\text{Insolinic acid.}}$$

The evolution of carbonic acid is readily demonstrated by experiment.

The formula $C_{18}H_8O_8$ has been confirmed by the analysis of several salts.

Silver-Salt.—This is separated in the form of a white amorphous curdy precipitate, on decomposing the ammonia salt by nitrate of silver. It requires long continued washing, together with careful exclusion of light. A combustion and several silver-determinations furnished the following results:

I.	0·3350 grm.	silver-salt	0·3348 carb. acid 0·0455 water, and 0·1835 silver
II.	0·3455	„	0·1891 silver
III.	0·4157	„	0·2274 „
IV.	0·3233	„	0·1778 „
V.	0·8030	„	0·4380 „
VI.	0·9710	„	0·7027 chloride of silver
VII.	0.1910	„	0·1380 „

These analytical results lead to the formula

$$C_{18}(H_6Ag_2)O_8$$

	Theory.		Experiment.							
			I.	II.	III.	IV.	V.	VI.	VII.	Mean.
C_{18}	108	27·41	27·25	—	—	—	—	—	—	27·25
H_6	6	1·52	1·507	—	—	—	—	—	—	1·507
Ag_2	216	54·82	54·77	54·73	54·70	54·99	54·54	54·46	54·34	54·64
O_8	64	16·25	—	—	—	—	—	—	—	—
	390	100·00								

Silver-determination VII., relates to a salt, the acid of which had been boiled for eight days with the oxidizing mixture, a proof that insolinic acid is not further changed in this manner. In this analysis, the acid which was separated on addition of nitric acid was likewise collected and weighed. 0·191 grm. silver-salt furnished 0·0865 grm. = 45·28 per cent. of acid, whilst 46·15 per cent. should have been obtained.

Copper-Salt.—A light blue salt, which is precipitated on mixing a neutral solution of insolinic acid with sulphate of copper. Analysis furnishes the following numbers:

I.	0·7805	copper salt	0·3185	oxide of copper
II.	0·7085	„	0·2885	„

according to which the precipitate appears to be a basic compound, probably

$$C_{18}(H_6Cu_2)O_8, HO, CuO$$

	Theory.	Experiment.	
		I.	II.
Copper	32·78	32·58	32·55

Barium-Salt.—Dilute solutions of insolinate of ammonium are not precipitated by salts of barium; on mixing concentrated solutions, a white, more or less crystalline, precipitate is produced, which may be washed with cold water. For analysis, the salt was dried at between 120° and 130° C, the barium was estimated as carbonate, and in one case as sulphate.

I.	0·4290	barium-salt	0·2700	carbonate of	barium
II.	0·2760	„	0·1728	„	„
III.	0·4045	„	0·2545	„	„
IV.	0·5210	„	0·3280	„	„
V.	0·6920	„	0·5115	sulphate of	barium.

These numbers correspond to the formula—

$$C_{18}(H_6Ba_2)O_8$$

	Theory.		Experiment.					
			I.	II.	III.	IV.	V.	Mean.
C_{18}	108	34·28	—	—	—	—	—	—
H_6	6	1·90	—	—	—	—	—	—
Ba_2	137	43·49	43·79	43·51	43·73	43·78	43·45	43·65
O_8	64	20·33	—	—	—	—	—	—
	315	100·00						

In a further analysis, VI., 0·356 barium-salt were decomposed by hydrochloric acid and the separated insolinic acid collected. It amounted to 0·2020 grm. = 56·74 per cent., whilst 57·14 per cent. of acid should have been obtained.

Calcium-Salt.—This is obtained as the barium-salt, which it also much resembles in its physical properties. When dried at 100° C, it contains—

$$C_{18}(H_6Ca_2)O_8 + 6\ Aq.$$

I.	0·504	calcium-salt	0·1870	carbonate of	calcium
II.	0·436	„	0·1645	„	„
III.	1·005	„	0·2000	„	„

	Theory.		Experiment.			
			I.	II.	III.	Mean.
C_{18} . .	108	39·70	—	—	—	—
H_6 . .	6	2·20	—	—	—	—
Ca_2 . .	40	14·70	14·84	15·08	—	14·96
O_8 . .	64	23·60	—	—	—	—
6 HO . .	54	19·80	—	—	19·90	19·90
	272	100·00				

The water escapes between 120° and 130° C; when dried at this temperature, the salt has the composition

$$C_{18}(H_6Ca_2)O_8$$

as demonstrated by the following determination:

0·800 salt gave 0·3735 carbonate of calcium.

	Theory.		Experiment.
C_{18} . .	108	49·54	—
H_6 . .	6	2·75	—
Ca_2 . .	40	18·35	18·67
O_8 . .	64	29·36	—
	218	100·00	

Potassium-Salts.—Of these there are two, one neutral and one acid.

(a.) Neutral Potassium-Salt.—This is precipitated as a crystalline powder, upon mixing the saturated solution of insolinic acid in aqueous potassa, with strong spirits of wine. When dry, the salt exhibits a remarkable satiny lustre.

Analysis furnished the following results:

I.	0·5280	potassium salt gave	1·002	potassiochloride of platinum
II.	0·3176	„ „	0·220	acid
III.	0·5280	„ „	0·366	„

The formula

$$C_{18}(H_6K_2)O_8$$

requires the following values:

	Theory.		Experiment. I.
C_{18}	108	42·19	—
H_6	6	2·34	—
K_2	78	30·46	30·36
O_8	64	25·01	—
	256	100.00	

Percentage of acid corresponding to the neutral potassium-salt:

Theory.	Experiment. II.	Experiment. III.
70·31	69·27	69·30

(b.) Acid Potassium-Salt.—This is formed by boiling the solution of the neutral salt with an excess of insolinic acid; from the hot filtered solution there separate, on cooling, small crystalline scales, which contain

$$C_{18}(H_7K)O_8$$

I have made a determination of the acid only. 0·4025 of the acid salt gave 0·3305 acid; percentage of acid corresponding to the acid potassium salt:

Theory.	Experiment.
82·56	82·11

Potassium-Sodium-Salt.—I have endeavoured to obtain additional evidence of the bibasic nature of insolinic acid, by producing a compound which should contain the two alkali-metals. On precipitating the solution of the acid potassium-salt with carbonate of sodium, a salt is thrown down, the analysis of which has actually led to the formula

$$C_{18}(H_6KNa)O_8$$

0·1955 potassium-sodium-salt gave 0·1985 potassiochloride of platinum.

	Theory.		Experiment.
C_{18}	108	45·00	—
H_6	6	2·50	—
K	39	16·25	16·16
Na	23	9·58	—
O_8	64	26·67	—
	240	100·00	

In the above potassium-determination, the insolinic acid, separated on addition of hydrochloric acid, was likewise collected.

0·1955 salt furnished 0·1456 acid.

Percentage of acid corresponding to the potassium-sodium-salt:

Theory.	Experiment.
75·0	74·47

Unfortunately it is not possible to obtain the preceding compound by crystallization; it might, therefore, be nothing but a mechanical mixture of the neutral potassium-salt and the neutral sodium-salt. Too much argumentative value must not therefore be attached to the analysis of this compound.

Under these circumstances, the study of insolinic ethers would be possessed of a special interest. The formation, however, of these ethers can only be accomplished with the greatest difficulty, in consequence of the insolubility of the acid. They were actually obtained by the action of iodide of ethyl on the silver-salt in sealed tubes, and likewise by treating the acid suspended in alcohol with hydrochloric acid, but not in quantity sufficient to admit of careful study. I can only affirm that there exist two ether-compounds, the one possessing acid properties, the other neutral; both may be separated by potassa, and probably contain

$$C_{18}[H_7(C_4H_5)]O_8$$
$$C_{18}[H_6(C_4H_5)_2]O_8$$

I have, however, no analytical evidence to offer for this assumption.

The following table comprises all the compounds of insolinic acid which have been analyzed:

Acid	$C_{18}\ H_8$	O_8
Silver-salt	$C_{18}\ (H_6\ Ag_2)$	O_8
Copper-salt	$C_{18}\ (H_6\ Cu_2)$	O_8 + HO, CuO (?)
Barium-salt	$C_{18}\ (H_6\ Ba_2)$	O_8
Calcium-salt—		
at 100° C	$C_{18}\ (H_6\ Ca_2)$	O_8 + 6 HO
at 130° C	$C_{18}\ (H_6\ Ca_2)$	O_8
Potassium-salt—		
neutral.	$C_{18}\ (H_6\ K_2)$	O_8
acid	$C_{18}\ (H_7\ K)$	O_8
Potassium-sodium-salt	$C_{18}\ (H_6\ K\ Na)$	O_8

It now only remained to examine the behaviour of insolinic acid and its compounds under the influence of heat. On rapidly heating these substances, an aromatic odour is evolved, strongly reminding one of benzoic compounds. In fact, benzoic acid and benzole are found in greater or less quantity among the distillation-products of insolinic acid. When an intimate mixture of insolinic acid and pumice stone is distilled rapidly over a naked flame, and the semi-crystalline deposit condensed in the neck of the retort is heated with boiling water, benzoic acid in rather considerable

quantities is dissolved, and crystallizes on cooling. The residue is insolinic acid, which has distilled unchanged. The nature of both substances was fixed by a number; that of benzoic acid by the determination of the silver in the silver-salt.

0·242 grm. silver salt gave 0·1188 silver.

Percentage of silver in benzoate of silver:

$$C_{14}(H_5Ag)O_4$$

Theory.	Experiment.
47·1	47·0

Insolinic acid was identified by the analysis of the barium-salt. In fact, determination VI., in the preceding analysis of the barium compound, refers to salt prepared with the sublimed acid.

On distilling a mixture of insolinic acid and caustic baryta, a transparent liquid passes over, carbonate of barium mixed with charcoal remaining in the retort. The liquid was identified as pure benzol, both by the determination of the boiling point and by its transformation into nitrobenzole and aniline.

The conversion of insolinic acid into benzol was effected on a rather extensive scale, for, in fact, I was by no means prepared for this metamorphosis.

Considerations to which I shall have to revert at the conclusion of this note, had led me to expect the production of toluol ($C_{14}H_8$) according to the equation—

$$\underbrace{C_{18}H_8O_8}_{\text{Insolinic acid.}} = 4CO_2 + \underbrace{C_{14}H_8}_{\text{Toluol.}}$$

Careful and repeated experiments have, however, satisfied me that insolinic acid does not furnish a trace of toluol under these circumstances. The molecule of the acid experiences a more profoundly pervading change, as is evident from the separation of the carbon. The transformation of insolinic acid into benzoic acid and benzol may be exhibited by the following equations—

$$\underbrace{C_{18}H_8O_8}_{\text{Insolinic acid.}} = 2HO + CO_2 + C_3 + \underbrace{C_{14}H_6O_4}_{\text{Benzoic acid.}}$$

$$\underbrace{C_{18}H_8O_8}_{\text{Insolinic acid.}} = 2HO + 3CO_2 + C_3 + \underbrace{C_{12}H_6}_{\text{Benzole.}}$$

The formation of insolinic acid from cuminic acid led to the examination of some allied bodies in the same direction.

Nitrocuminic acid, boiled for several days with chromate of potassium and sulphuric acid, did not exhibit the slightest alteration. The homologous benzoic acid was not attacked by the oxidising mixture, even after having been boiled with it for weeks. Toluylic acid,

standing, as it does, between benzoic and cuminic acid, appeared to promise a different result. Toluylic acid was, as is well known, produced by Noad, on submitting cymol (the hydro-carbon accompanying the aldehyde of cuminic acid in Roman cumin oil) to dilute nitric acid. The preparation of toluylic acid, by means of nitric acid, is, however, an extremely irksome and tedious operation. It is necessary to employ the nitric acid so extremely dilute as hardly to act on the hydrocarbon; otherwise, nitrotoluylic acid only is obtained. I had hoped to arrive at a more rapid result by the action of the chromic oxidising mixture. In fact, cymol is energetically attacked by this mixture; but the acid which is formed is not toluylic, but insolinic acid,—the same acid which was produced from cuminic acid.* Determination III. and IV., to be found in the analysis of insolinate of barium, refer to salts obtained from insolinic acid prepared from cymol. This observation indicates a simple method of easily procuring insolinic acid in considerable quantity. It is only necessary to heat the ordinary Roman cumin-oil (cymol and cuminol), with a mixture of chromate of potassium and sulphuric acid. It is, however, necessary to apply the heat very slowly, and to be provided with the means of cooling rapidly, otherwise much oil may be lost, in consequence of the extraordinary energy of the action.

The preceding researches suggested some additional experiments, the results of which I will here briefly mention.

When cumol is boiled for some time, with a mixture of sulphuric acid and chromate of potassium, it is readily and completely converted into benzoic acid, exhibiting, under these circumstances, the same behaviour which is observed on heating it with dilute nitric acid.

The oxidation-products of toluol have already been examined by Deville,† who found that this hydrocarbon is likewise converted into benzoic acid. But this chemist succeeded only once in obtaining benzoic acid from toluol; and, since the toluol he employed was procured from balsam of tolu, which, as is well known, furnishes a considerable quantity of benzoic acid, he did not regard the experiment as conclusive. I have, therefore, repeated the experiment with toluol prepared from coal-gas naphtha. The action of the oxidizing mixture is slow; but the transformation was repeatedly and easily effected. The identity of the benzoic acid obtained by this method was fixed by a number.

0·251 silver salt left 0·1175

Percentage of silver in benzoate of silver:

$C_{14}(H_5Ag)O_4$

Theory.	Experiment.
47·1	46·8

* It is conceivable that in a first stage of this reaction the toluylic acid is actually formed. I have not varied the experiment sufficiently to offer a decided opinion on this subject.

† Ann. Ch. Phys. [3], III. 171.

When considered by itself, insolinic acid has but slight claims on the attention of chemists; but when viewed in connection with other groups of bodies, it acquires increased interest. Some years since, Gerhardt pointed out, that to the homologous series of *monobasic fatty acids*, $C_{2n}H_{2n}O_4$, the lowest terms of which are formic and acetic acid, there runs parallel a homologous series of bibasic acids $C_{2n}H_{2n-2}O_8$, the simplest member of which is oxalic acid. These two series of acids are connected by the closest ties, and very conclusive experiments have demonstrated that the members of the former may be easily converted into those of the latter. Such is the case of the transformation of butyric into succinic acid, effected by M. Dessaignes, by means of oxidizing agents.

The following table exhibits these two series of acids arranged according to their carbon:

Formic acid	$C_2H_2O_4$	——	
Acetic acid	$C_4H_4O_4$	Oxalic acid	$C_4H_2O_8$
Propionic acid	$C_6H_6O_4$	— ?	$C_6H_4O_8$
Butyric acid	$C_8H_8O_4$	Succinic acid	$C_8H_6O_8$
Valeric acid	$C_{10}H_{10}O_4$	Pyrotartaric acid	$C_{10}H_8O_8$
Caproic acid	$C_{12}H_{12}O_4$	Adipic acid	$C_{12}H_{10}O_8$
Œnanthylic acid	$C_{14}H_{14}O_4$	Pimelic acid	$C_{14}H_{12}O_8$
Caprylic acid	$C_{16}H_{16}O_4$	Suberic acid	$C_{16}H_{14}O_8$
Pelargonic acid	$C_{18}H_{18}O_4$	— ?	$C_{18}H_{16}O_8$
Rutic acid	$C_{20}H_{20}O_4$	Sebacic acid	$C_{20}H_{18}O_8$

The existence and the mode of formation of insolinic acid prove that to the series of *monobasic aromatic acids*, $Cn_2Hn_{2-8}O_4$, the lowest term of which is benzoic acid, there corresponds likewise a series of bibasic acids, $C_{2n}H_{2n-8-2}O_8 = C_{2n}H_{2n-10}O_8$. Of this series few members are at present known; but the group of aromatic acids is itself very imperfect and limited. The two series comprise at present the following terms:

Benzoic acid	$C_{14}H_6O_4$	?	$C_{14}H_4O_8$
Toluolic acid	$C_{16}H_8O_4$	Terephthalic acid Phthalic acid	$C_{16}H_6O_8$
? —	$C_{18}H_{10}O_4$	Insolinic acid	$C_{18}H_8O_8$
Cuminic acid	$C_{20}H_{12}O_4$	?	$C_{20}H_{10}O_8$

It is evident that the carbon being made the standard of comparison, the bibasic insolinic acid corresponds to the monobasic acid, which stands between toluylic and cuminic acid, and which is at present unknown.*

In addition to this unknown acid, toluylic acid is represented in the series of bibasic acids. There are, in fact, two bodies which

* Benzo-glycolic acid, formed by the action of nitrous acid on hippuric acid, has the same composition as insolinic acid; but it is monobasic, and differs, moreover, from insolinic acid by its physical properties.

may be regarded as representations of toluylic acid. These are phthalic acid, and a compound which Caillot* produced by oxidizing oil of turpentin by means of nitric acid, and which he has described under the name of terephthalic acid.† Both acids contain $C_{16}H_6O_8$; both are bibasic; both are decomposed under the influence of heat, or, more perfectly by heating with baryta, into carbonic acid and benzol. But, notwithstanding this similarity, both are positively distinct chemical substances; for, while phthalic acid is soluble in water and alcohol, and may be obtained from these liquids in definite crystals, terephthalic acid is scarcely attacked by these solvents, and forms at best an indistinctly crystalline powder. Moreover, phthalic acid, like the bibasic acids, corresponding to the series $C_{2n}H_{2n}O_4$, loses two equivalents of water when submitted to the action of heat, easily forms amidogen-compounds, and may without difficulty be converted into a nitro-substitute. All these properties are absent in terephthalic acid. I have here purposely compared the properties of these two acids, in order to show that terephthalic acid in its entire deportment resembles closely insolinic acid; whilst phthalic acid, in its behaviour, solubility, crystallization, dehydratability, and power of forming amidogen-compounds, approaches nearer the bibasic acids of the series which runs parallel with the fatty acids. It is conceivable that phthalic acid is the true representative in the series of bibasic aromatic acids ($C_{2n}H_{2n-10}O_8$), and that the homologues, terephthalic, and insolinic acids have to be viewed as acids isomeric with the members of the former series, whose analogues for the bibasic fatty acids are not yet discovered.

* Ann. Chem. Phys. [3], xxi. 30.

† Caillot's memoir on oil of turpentine was published ten years since, and obviously contains several statements which require confirmation. I therefore thought it desirable to repeat these experiments, so far at least as they related to terephthalic acid. By following exactly the method indicated by Caillot, a small quantity of an insoluble, somewhat coloured, acid was ultimately obtained, the barium- and silver-salts of which resembled the corresponding compounds of insolinic acid. On analysis, these salts furnished numbers representing pretty accurately terephthalic acid.

0·263 barium salt; 0·2024 sulphate of barium

$C_{16}(H_4Ba_2)O_8$

	Theory.	Experiment.
Barium	45·51	45·24

0·190 silver salt; 0·1073 silver

$C_{16}(H_4Ag_2)O_8$

	Theory.	Experiment.
Silver	56·84	56·46.

On Lophine.*

By A. Gössmann and E. Atkinson.

Among the products of decomposition formed by heating hydrobenzamide to a high temperature, Laurent† found, besides amarone, a new base, to which he gave the name lophine. At first he proposed for it the formula $C_{46}H_{17}N_2$, and afterwards $C_{46}H_{16}N_2$.

About the same time, Fownes obtained, by the dry distillation of amarine (the benzoline of Fownes), a substance possessing weak basic properties, to which he gave the name pyrobenzoline, and the composition of which he expressed by the formula $C_{21}H_8N$.

It was observed by one of us‡ that lophine was formed when the compound of bisulphite of ammonia with oil of bitter almonds is heated with dry hydrate of lime. This led us to examine the base, on the one hand with a view to establish its true formula, and on the other to ascertain if any connection existed between the lophine of Laurent and the pyrobenzoline of Fownes.

The results of our investigation determine us to adopt for lophine the formula $C_{42}H_{17}N_2$; and have further led us to the conviction that pyrobenzoline is identical with lophine.

In the paper above cited, which describes the formation of lophine and amarine from the compound of oil of bitter almonds and bisulphite of ammonia, it was mentioned that the formation of lophine was greatly promoted by rapidly heating the mixture to a temperature of 250° to 300° C. It being our object to obtain as large a product of lophine as possible, we endeavoured to ascertain the conditions for the fulfilment of this object. We found that by mixing with the hydrate of lime its weight of caustic lime, and by covering the retort as far as it was filled with the mixture, with live coals, from the beginning of the operation, the greatest product was obtained. An apparatus constructed as follows proved very convenient. A shallowish globular retort was coated with clay, to about the height to which the fire was to be piled up. The neck of the retort, cut off to six inches in length, was inserted in a tubulated cylinder, which served as a receiver. In the tubulure of the cylinder a tube bent twice at right angles was inserted, the other end of which dipped into water. In this manner it was possible to observe the occurrence of any volatile oily products as well as gases. The greatest products were

* Ann. Ch. Pharm. xcvii, 283.
† Revue Scientifique, No. 56; J. pr. Chem., xxxv., 455.
‡ Ann. Ch. Pharm., xciii., 331.

obtained when small quantities were operated upon; 10 to 15 grammes of the oil of bitter almonds compound with about four to six times the quantity of the lime mixture appeared to be the best proportions for one operation. If the operation be conducted as above indicated, only a small quantity of amarine is formed at first. When this has melted down, the upper part of the retort begins to be covered with radiant masses of lophine, the formation of secondary products ceases, and there seems only to be formed, besides lophine, some free ammonia. At the beginning, a small quantity of an aromatic oily product accompanies the lophine. But this only appeared to result from amarine, which, at the beginning of the operation, had settled in the upper part of the retort, and which, by the rapidly increased heat, had been decomposed into lophine and some products which have not been closely examined. Of these, the principal appears to be *amarone*. This body, described by Laurent, is only distinguished from lophine by its differing solubility in ether and alcohol, but contains 88·4 p.c. of carbon. It is apparently to the presence of small quantities of this substance, that the conflicting analyses of lophine must be ascribed. We have the more reason to ascribe these discrepancies to this cause, inasmuch as different preparations of lophine obtained by the above process, in which the occurrence of secondary products is reduced to a minimum, and purified as follows, gave us well agreeing analytical results.

The lophine which we used for analysis and for the preparation of the various salts was thus purified. In order to free the crude product of distillation from adhering amarine and oily and colouring admixtures, it was digested several times with moderately strong alcohol. It was then dissolved in boiling alcohol, to separate any lime which might have been mechanically carried over, boiled for some time with animal charcoal, and filtered. On standing, tuft-shaped masses of long needles separated out, and the mother liquid was evaporated as long as any of these were formed. These crystals, separated from the mother-liquors, were dissolved in alcohol acidulated with hydrochloric acid, the solution precipitated boiling by aqueous ammonia, and the base repeatedly crystallized from alcohol.

The base thus purified exhibited the following properties. From an alcoholic solution it crystallizes in tufted-grouped needles often an inch long, and possessing a lustre similar to that of caffein. The crystals, which at first are transparent, become opalescent, but retain their lustre. The crystals are tasteless and inodorous; scarcely exhibit any alkaline reaction; are difficultly soluble in ether, more so in alcohol, and very little in water. Heated to 250° C. they sublime gradually without leaving any residue, and without melting. They melt at 265° C. to a clear transparent mass, which at 260° C. solidifies to a

radiating crystalline mass. They sublime in a form similar to that of benzoic acid.

The alcoholic solution of the base, and particularly of the sulphate and hydrochlorate, exhibit the phenomenon of fluorescence similarly to quinine, though not in so high a degree. But, unlike that base, lophine effects no rotation of the plane of polarization.

The analyses of lophine purified as above, and of various preparations, gave the following numbers:

I.	0·2966	gave	0·9225	CO_2	and	0·152 HO
II.	0·2610	„	0·8107	CO_2	„	0·1327 HO
III.	0·2396	„	0·7445	CO_2	„	0·1250 HO
IV.	0·2449	„	0·7606	CO_2	„	0·1245 HO
V.	0·3235	„	1·0031	CO_2	„	0·1630 HO
VI.	0·2325	„	——	—	„	0·1188 HO
VII.	0·343	afforded on treatment with soda-lime, &c., 0·5184 $NH_4Cl + PtCl_2$.				

The formula hitherto proposed, partly on analytical data and partly on theoretical grounds, are as follows:

	I. Laurent.	II. Laurent.	Fownes.	List (Gmelin's Handbuch, vi. 157).
	$C_{46}H_{17}N_2$	$C_{46}H_{16}N_2$	$C_{21}H_8N$	$C_{44}H_{16}N_2$
C	85·98	86·25	85·13	85·75
H	5·29	5·00	5·41	5·19
N	8·72	8·75	9·46	9·09

We propose the formula $C_{42}H_{17}N_2$, and subjoin the calculated analytical results:

	Calculated.	Found.							Mean.
		I.	II.	III.	IV.	V.	VI.	VII.	
C_{42}	84·84	84·82	84·71	84·74	84·84	84·56	—	—	84·73
H_{17}	5·72	5·69	5·65	5·79	5·35	5·60	5·70	—	5·63
N_2	9·42	—	—	—	—	—	—	9·47	9·47

The carbon, which has most influence on the formula, agrees best with our analyses. In order to ensure complete combustion, we used tubes six inches longer than is usual in combustion with oxide of copper and oxygen. To prevent the formation of any oxides of nitrogen, sheet copper was placed at the anterior part of the tube.

The identity of the pyrobenzoline of Fownes with the lophine of Laurent has been already suggested by Gerhardt.* And, indeed, after Bertagnini† had shown that hydrobenzamide could be converted into amarine by simply heating it, there could be little doubt about it. A direct proof only was needed. Our observations of the properties of lophine, as detailed above, agree perfectly with Fownes's description of pyrobenzoline. And the

* Traité de Chimie Organique, tome iii., 179.
† Liebig's Annalen.

analyses of this chemist agree well with our own. As he did not examine the nature of the base more closely, he could only give as a formula the simplest expression of his analytical results. On doubling his formula, it only differs by one equivalent of hydrogen from our own.

Lophine is a very weak base, and has scarcely any alkaline reaction. It forms, indeed, well characterised salts, but these have a tendency, on recrystallization, to give up part of their acid, and become changed into basic compounds. This is particularly the case with the sulphate.

Hydrochlorate of Lophine = $C_{42}H_{17}N_2 + HCl + HO$. If to a hot saturated alcoholic solution of lophine, hydrochloric acid be added till the mixture is decidedly acid, the hydrochlorate separates out, on cooling, in large transparent needles, very similar to pure lophine. If these crystals be allowed to stand for some time in the acid mother-liquor, they change into small, white, opaque prisms. We have observed this to be the case with several lophine compounds. It is possible that the change depends on some loss of water, for we could ascertain no essential difference in the comportment of this form of the salt. If the base be treated directly with concentrated hydrochloric acid, it becomes resinous, and can only be obtained in the crystalline state by removing the excess of acid, and recrystallization from alcohol.

The hydrochlorate has a feebly acid reaction. It is more soluble in alcohol and water, and shows the fluorescent appearance more strongly than the pure base.

The analyses afforded the following results:

I. 0·272 gave 0·736 CO_2 and 0·1355 HO
II. 0·1984 „ 0.538 CO_2 „ 0·1010 HO
III. 0·2184 „ 0·0834 Ag Cl.

	Calculated.	Found.		
		I.	II.	III.
C	42 = 73·57	73·78	73·80	—
H	19 = 5·54	5·51	5·65	—
N	2 = 8·17	—	—	—
Cl	1 = 10·36	—	—	9·42
O	1 = 2·33			

Hydriodate of Lophine, $C_{42}H_{17}N_2 + HI$. This salt is obtained in the same manner as the hydrochlorate. It crystallizes easily in large needles, which are more soluble in alcohol and ether than the hydrochlorate. It crystallizes from a very acid solution in granular crystals. Hydriodate of lophine is very soluble in iodide of ethyl. Its other properties are exactly similar to those of the hydrochlorate.

Sulphate of Lophine, $C_{42}H_{17}N_2 + HO, SO_3$? When a solution of lophine, to which excess of sulphuric acid has been added, is

allowed to evaporate slowly, the sulphate separates out in the form of broad, transparent, rhombic tables, which are often 4 or 5 lines in length and 2 lines in breadth. On standing in the air, they become opaque and effloresce. When crystallized more rapidly, the compound separates out in the form of large needles, which, on standing some time in the acid mother-liquor, change into small white opaque needles. At each recrystallization from alcohol, the salt becomes more basic, a phenomenon which appears to have been observed by Laurent; at least, some of his analyses allow of this assumption. By frequent solution and recrystallization from water, the sulphuric acid may be almost entirely removed from the compound, as our analyses have convinced us. The analytical results which we have obtained exhibit, from this reason, great variation, and we have not thought it necessary to adduce them.

Nitrate of Lophine, $C_{42}H_{17}N_2 + HO, NO_5$. This salt crystallizes from a concentrated alcoholic solution of lophine, which has been acidulated with nitric acid, in the form of small plates. If these be covered with concentrated nitric acid which is free from nitrous acid, they become converted into an oily mass. In other particulars we can confirm Laurent's description of this salt.

Hydrochlorate of Lophine and Bichloride of Platinum, $C_{42}H_{17}N_2 HCl + Pt Cl_2$. This double salt is formed on mixing a dilute alcoholic solution of bichloride of platinum with a warm moderately concentrated solution of lophine containing excess of hydrochloric acid. On cooling, crystals which are often needle-shaped separate out, and these, on standing, sometimes crumble to a beautiful orange-yellow crystalline powder. This salt is more soluble in alcohol than any other compound of lophine. If an alcoholic solution of lophine be heated some time with excess of bichloride of platinum, the base becomes essentially altered. Platinum is separated in a very finely divided state, and the liquid filtered off from this is very difficult to crystallize. The body which separates out is generally soft, adhering together in a resinous mass, and the quantity of platinum in it is less than in the crystallized double salt. The analysis of the double salt gave us the following numbers:

I. 0·3280 gave 0·5920 CO_2 and 0·116 HO
II. 0·2250 „ 0·0445 Platinum.

	Calculated.	Found.	
		I.	II.
C_{42}	50·08	49·22	—
H_{18}	3·58	3·93	—
N_2	5·56	—	—
Cl_3	21·16	—	—
Pl_1	19·61	—	19·77

Bichloride of platinum unites also directly with lophine. When a concentrated alcoholic solution of lophine is mixed with a concentrated, neutral, alcoholic solution of bichloride of platinum, a clear, orange-yellow, microscopic crystalline compound separates, which seems to be a compound of $4(C_{42}H_{17}N_2) + 3PtCl_2$. A compound thus constituted would require 17·45 per cent. of platinum; our analyses give the following numbers:

I.	0·3450 gave	0·0605 Pt = 17·53	per cent.
II.	0·2540 „	0·0504 Pt = 17·27	„
III.	0·3515 „	0·0610 Pt = 17·35	„

Lophine and Nitrate of Silver.—If a neutral, moderately concentrated, alcoholic solution of nitrate of silver be mixed with a hot, saturated, alcoholic solution of lophine, the mixture solidifies on cooling to a mass of crystals. If these be dissolved in cold alcohol, and left to spontaneous evaporation, the compound separates in tolerably large white needles, which on analysis gave numbers corresponding to the above formula. But on attempting to purify the compound by recrystallization, it changes by boiling into a pulverulent, crystalline, difficultly soluble substance, which settles down with a somewhat violet tint. This compound is thus constituted:

$$2C_{42}H_{17}N_2 + 3(Ag\,O, NO_5)$$

0·2295 gave 0·0666 Ag = 29·01 per cent. The above formula requires 29·36 per cent. After separating this body, and further evaporation of the mother-liquor, another and more soluble compound crystallizes out, in brilliant white needles. It has the formula

$$2C_{42}H_{17}N_2 + Ag\,O, NO_5$$

0·2800 gave 0·039 Ag = 13·92 p.c. The above formula requires 14·14.

The change effected on boiling may be thus expressed:

$$4(C_{42}H_{17}N_2 + Ag\,O, NO_5) = 2C_{42}H_{17}N_2 + 3(Ag\,O, NO_5) + 2C_{42}H_{17}N_2 + Ag\,O, NO_5.$$

In order to get a clearer view of the process of the formation of lophine, we endeavoured to ascertain its constitution, and to see to what class of artificial bases it belonged. To this end, various attempts to substitute ethyl were made, by treating it with iodide of ethyl. Pure lophine was enclosed in a glass tube with alcohol and excess of iodide of ethyl, in which it was abundantly soluble, and left for some weeks. Another portion of lophine, which had also been enclosed with iodide of ethyl and alcohol, was heated for three or four days to 100° C., and then left to stand some weeks. Both portions were examined separately, but showed the same phenomena. The contents of the tubes had an acid reaction, arising from hydriodic acid. After the excess of iodide

of ethyl had been distilled off, a readily soluble hydriodate separated in fine needles. This was recrystallized from alcohol, and one portion treated with oxide of silver. Another portion was treated with ammonia. In both cases the substances obtained afforded analytical results perfectly agreeing with the composition of pure lophine. Hence, under these circumstances, no substitution had taken place. A portion of the iodide of ethyl had decomposed into alcohol and hydriodic acid, which united with the lophine to form a hydriodate. A similar phenomenon was observed by How,* when narcotine and several other bases were similarly treated.

Examination of select Vegetable Products from India.

By John Stenhouse, L.L.D., F.R.S.

Read before the Royal Society, December 6, 1855.

PART I.

Through the kindness of my esteemed friend Dr. Royle, I have been permitted to select such vegetable products from the extensive collection at the India House as seemed most likely to repay the trouble of investigation. My attention during the last twelve months has been chiefly directed to three of these vegetable substances; and the results of their examination I now take the liberty of submitting to the Royal Society, to be followed by those of the others as they may be completed.

Datisca Cannabina.

The first of these substances which I examined consisted of a quantity of the roots of the *Datisca cannabina*, from Lahore, where this plant is employed to dye silk of a fast yellow colour. The roots, which had been cut into pieces about six or eight inches long, were from one-half to three-quarters of an inch in thickness. They had a deep yellow colour. The leaves and smaller branches of the *Datisca cannabina* from the Levant have long been employed for a similar purpose in the south of France. A decoction of the leaves of the *Datisca cannabina* was examined by Braconnot in 1816, who discovered in it a crystallizable principle to which he gave the name of *datiscine*. Braconnot, of course, did not subject this substance to analysis, but he described its appearance and

* Transactions of Edin. Royal Society, 21, 1.

properties in an exceedingly accurate manner.* The observations of Braconnot had fallen into such entire oblivion, however, that for many years past, we find in most of the larger systems of chemistry the term *datiscine* used as synonymous with *inuline*. Thus in Brande's 'Chemistry,' vol. ii. page 1168, we find it stated that a variety of names had been given to inuline, such as "dahline, datiscine," &c. In Löwig's 'Chemistry of Organic Compounds,' vol. i. page 359, the same error is repeated, where, under the article "inuline," the synonyms given are "dahline and datiscine."

The bruised roots were extracted in a Mohr's apparatus by long-contiued digestion with wood-spirit. The liquor obtained, which had a dark brown colour, was concentrated by distilling off a portion of the wood-spirit. The brown syrupy liquid remaining in the retort, on being poured into open vessels and standing for some time, deposited a resinous matter containing merely traces of a crystalline substance. When this syrupy liquid, however, was treated with about half its bulk of hot water, the greater portion of the brown resin was rapidly deposited; and the mother-liquor, having been poured off and left to slow spontaneous evaporation, deposited a considerable quantity of an imperfectly crystallizable substance resembling grape-sugar. These crystals are impure *datiscine*, still retaining a considerable amount of resinous matter, to which the dark brown colour is owing.

They may be purified in various ways, advantage being taken of the greater solubility of the resinous matter in alcohol or ether, than that of the datiscine. By repeated crystallizations, therefore, from either of these liquids, the datiscine may be rendered almost perfectly colourless, the impurities remaining in the mother-liquor. The following is the method which I have found, on the whole, most convenient. The crude datiscine, while still moist, is strongly pressed between folds of blotting-paper; it is then dissolved in alcohol, and again treated with water, which throws down the resin. The diluted alcoholic solution, after standing some time, yields the datiscine in a much finer state. On repeating this operation several times, the datiscine may be obtained perfectly pure. In order to separate any traces of tannic acid which might have been present, I repeatedly added a concentrated solution of gelatine to the alcoholic solution of the datiscine, and after careful filtration, precipitated the datiscine in the way already described. I could not, however, observe that the crystals of the datiscine, when gelatine had been employed in its preparation, were in the least degree dissimilar from the datiscine obtained in the usual way.

Properties of Datiscine.—Datiscine, when quite pure, is perfectly colourless; but, unless great attention is paid to its purification, it

* Ann. Ch. Phys. [3], iii. 277.

usually has more or less of a yellow colour, varying from pale to deep yellow, according to circumstances. It is very soluble in alcohol, even in the cold, boiling alcohol dissolving almost any amount of it.

By slow spontaneous evaporation, its alcoholic solutions yield small silky needles arranged in groups. Cold water does not dissolve much of it, but it is tolerably soluble in boiling water, the hot solutions on cooling depositing it in shining scales. Ether does not dissolve much datiscine; but an ethereal solution, when allowed to evaporate as slowly as possible, yielded it in larger crystals than I could have obtained in any other way. When water is added to an alcoholic solution of datiscine, no precipitate is immediately formed, unless the solution is greatly concentrated; but on standing for some time, the datiscine separates in a very pure state, consisting of fine crystals having a pale yellow colour. The datiscine prepared by this process was found to contain but a minute trace of ash. When datiscine is heated to about 180° C., it melts, and if the heat is still further increased, it burns, evolving an odour of caramel, and leaves a voluminous charcoal. If datiscine be heated in a close vessel while a stream of dry air is slowly passed over it, a small quantity of a crystalline substance sublimes. Datiscine and its solutions have a very bitter taste; and though it does not produce any change upon test paper, I think there is reason to regard it as a feebly acid body. It dissolves in solutions of the fixed alkalies and ammonia, as well as in lime and baryta water. Their solutions have a deep yellow colour, which they lose on the addition of an acid, when the datiscine is precipitated, even acetic acid precipitating datiscine. When its alkaline solutions are not too concentrated, and are neutralized while hot, the datiscine on cooling is deposited in small crystals. The aqueous solution of datiscine is precipitated by neutral and basic acetates of lead, or chloride of tin. These precipitates have a bright yellow colour.

Salts of copper produce greenish precipitates; those of peroxide of iron deep brownish-green precipitates. The datiscine employed in these experiments had been purified with gelatine.

The lead salts form such gelatinous precipitates, that they could not be washed, and therefore I was unable to employ them in determining the equivalent of datiscine.

Action of dilute Sulphuric Acid on Datiscine. — When an aqueous solution of datiscine is treated with a small quantity of sulphuric acid, the clear liquid, after being boiled for a few minutes, becomes turbid, and deposits a crystalline substance. This is collected on a filter, and the clear liquid which passes through, after it has been made strongly alkaline by the addition of potash, and after being heated to 212°, throws down suboxide of copper. When the excess of sulphuric acid is removed from

another portion of the solution, by neutralizing with carbonate of lead or baryta, it acquires a sweet taste; and when evaporated to the consistence of a syrup, on standing for some time, it formed a semi-crystalline mass, closely resembling honey. This experiment showed, therefore, that datiscine, like salicine and similar bodies, belongs to the class of glucosides, and is a copulated compound of sugar and another substance which I shall call *datiscetine*.

Datiscetine.—Datiscetine in its general appearance and properties closely resembles datiscine. On a closer examination, however, these two substances are found to differ essentially, both in composition and properties. Datiscine, when prepared by boiling a solution of pure datiscine with dilute sulphuric acid, precipitates in the state of fine needles, which are nearly colourless. It is easily soluble in alcohol, a hot alcoholic solution, on cooling, depositing the greater portion of it in crystalline groups. It is almost insoluble in water, and consequently datiscetine is abundantly precipitated from its alcoholic solutions by the addition of water. It dissolves in ether to almost any extent, and is deposited, on the evaporation of that liquid, in needles.

These properties of datiscetine enable us to obtain it in a tolerably pure state, when even very impure datiscine is employed in its preparation. The mother-liquors out of which datiscine has been crystallized, and which retain a large amount of impurities, can be used in the following way for the preparation of datiscetine. These liquors are first treated with basic acetate of lead, the precipitate is collected on a filter and washed, and then, having been distributed through water, is decomposed by sulphuretted hydrogen. The solution which has filtered from the precipitated sulphide of lead, is then concentrated, and boiled with dilute sulphuric acid. The datiscetine produced in this way can be easily separated from the resinous matter, as the latter is precipitated before the formation of the datiscetine by the acid, and adheres to the bottom of the flask. By dissolving the datiscetine thus obtained in alcohol, and precipitating it by the addition of water, it is rendered tolerably pure.

Properties of Datiscetine.—Datiscetine has no taste. When heated it melts like datiscine, but the heat required is much higher than is necessary for that body. It crystallizes again on cooling. By operating very cautiously, a portion of the datiscetine may be sublimed in crystals. This sublimate, however, appears to be altered datiscetine, for, when recrystallized out of ether, it has a sweet taste. Datiscetine on burning does not emit the smell of caramel.

Datiscetine, like datiscine, dissolves in alkaline solutions, and is reprecipitated by the addition of an acid. When an alcoholic solution of acetate of lead is added to one of datiscetine, also dissolved in alcohol, a finely coloured deep yellow precipitate is

obtained, which can be easily washed both by alcohol and water.

This precipitate gave, by analysis, results agreeing with the formula $C_{30}H_8O_{10} + 2PbO$.

	Required.		Found.		
C_{30}	= 180·0	36·63	36·11	—	36·09
H_8	= 8·0	1·63	1·69	—	1·61
O_{10}	= 80·0	16·28	—	—	—
$2PbO$	= 223·4	45·46	45·22	45·13	45·73
	491·4	100·00			

Analysis of Datiscetine.—The different preparations were all dried at 100° C. in a current of dry air, and burned in the gas furnace. I. and II. were crystallized from alcohol; III. and IV. were precipitated from the alcoholic solution by water.

	Required.		Found.			
			I.	II.	III.	IV.
C_{30}	= 180	62·94	62·89	62·90	62·88	63·03
H_{10}	= 10	3·49	3·58	3·70	3·61	3·76
O_{12}	= 96	33·57	—	—	—	—
	286	100·00				

Analysis of Datiscine dried in a Liebig's *drying tube.*—A. Datiscine crystallized out of alcohol. B. Datiscine crystallized out of alcohol from another preparation. C. Datiscine prepared with gelatine and out of alcohol. D. Datiscine separated from its alcoholic solution by the addition of water. E. Datiscine precipitated from its potash solution by the addition of acetic acid.

The substance analysed in A. contained 0·3 to 0·4 per cent. of ash; that in B. 0·2 to 0·25 per cent.; and that in C. 0·12 per cent. No allowance, however, was made for these amounts of ash in calculating the following numbers.

The datiscine used for the analyses D. and E. did not contain any appreciable quantity of ash.

	A.		B.		C.	D.		E.
C .	54·79	54·38	54·79	54·73	54·97	54·11	54·48	54·27
H .	5·08	5·19	5·25	5·29	5·16	5·41	5·19	5·12
O .	—	—	—	—	—	—	—	—

When the decomposition of datiscine into datiscetine and sugar is taken into consideration, it seems probable that the formula for datiscine is

$$\text{Datiscetine} + \text{Sugar} = \text{Datiscine}$$
$$C_{30}H_{10}O_{12} + C_{12}H_{12}O_{12} = C_{42}H_{22}O_{24}.$$

That formula requires

$C_{42} = 252$	54·08
$H_{22} = 22$	4·72
$O_{24} = 192$	41·20

If the formula $C_{42}H_{22}O_{24}$ be correct, the decomposition of datiscine would be analogous to salicine, which, when treated with dilute acid, gives

$$\text{Salicine} = \text{Sugar} + \text{Salicetine}$$
$$C_{26}H_{18}O_{14} = C_{12}H_{12}O_{12} + C_{14}H_6O_2;$$

whilst when treated with emulsine,

$$\text{Salicine} = \text{Sugar} + \text{Saligenine} - 2\text{HO}.$$
$$C_{26}H_{18}O_{14} = C_{12}H_{12}O_{12} + C_{14}H_8O_4 - 2\text{HO}.$$

The above formula for datiscine is confirmed by the following determinations of sugar formed by treating a weighed quantity of datiscine with dilute sulphuric acid. The quantity of sugar produced was estimated by Fehling's method with a standard solution of sulphate of copper. Four determinations made in this way gave, for 100 parts of dry datiscine, 41·6, 39·5, 39·3, and 37·8 parts of sugar. The calculation for the formula $C_{42}H_{22}O_{24}$ requires 38·6 per cent. of sugar.

An attempt was made to confirm these determinations by the direct estimation of the datiscetine formed during the decomposition of a given weight of datiscine by dilute sulphuric acid. The numbers obtained, however, during different experiments did not correspond with each other, and were all much lower than theory required. This, however, is not to be wondered at, as the datiscetine, though very difficultly soluble, is by no means absolutely insoluble in water. Dilute hydrochloric acid was found, like sulphuric acid, to decompose the datiscine into sugar and datiscetine, and even on boiling an aqueous solution of pure datiscine for some hours, traces of sugar could be detected; thus showing that a small portion of the datiscine had been decomposed. It has been shown by previous experiments, and analysis No. 8, that datiscine may be dissolved in cold solutions of potash without decomposition. When boiled, however, with a concentrated potash-ley for some time, decomposition takes place, and the precipitate, thrown down by the addition of an acid, has all the properties of datiscetine. In this respect, therefore, datiscine agrees with tannin and similar glucosides, which yield the same products when acted upon by acids and alkalies; tannin from nut-galls being equally resolved by acid and alkalies into gallic acid and grape-sugar. A solution of datiscetine, when left for some time in a warm place in contact with yeast, did not ferment; and though emulsine was also tried, no separation of datiscetine was observed.

Action of Nitric Acid on Datiscine and Datiscetine.—When datiscetine is treated in the cold with nitric acid of ordinary strength, a violent reaction takes place, brown vapours are disengaged, and a resinous substance produced. The heat evolved by the reaction is sufficient to continue it till all the resinous matter is dissolved and a dark red liquid produced, which after boiling becomes yellow, and when cautiously evaporated, deposits on cooling crystals of nitropicric acid. If the reaction is not carried too far, no oxalic acid is formed, and the nitropicric acid obtained is very pure, forming large crystals of a pale yellow colour. The following experiments show that these crystals are really nitropicric acid.

When treated in the cold with a concentrated solution of hypochloride of lime, the very characteristic smell of chloropicrine is instantaneously observed. The addition of a solution of potash to a second portion of the acid threw down crystals of very pure nitropicrate of potash, which, when subjected to analysis, gave 18·04 per cent. of potash, the calculated quantity required for nitropicrate of potash being 17·66 per cent. Datiscine treated in the same way yields nitropicric acid as well as oxalic acid. The formation of nitropicric acid by the action of strong nitric acid on datiscine and datiscetine, renders it highly probable that, by employing dilute nitric acid, less highly oxidized products of decomposition might be obtained. Datiscetine was therefore boiled with dilute nitric acid, *i. e.*, nitric acid with ten parts of water; the crystals of datiscetine soon dissolved, and a yellow liquid was obtained, which, when treated with a solution of perchloride of iron, gave a blood-red colour. When the original solution had cooled, pale yellow crystals were deposited. These crystals were very soluble in hot water, and recrystallized on cooling.

They were likewise very soluble in alcohol and ether, and, when deposited by slow evaporation from their alcoholic solutions, they formed nearly colourless crystals of considerable size, having a fine silky lustre. When treated with hypochlorite of lime, they did not evolve chloropicrine in the cold, but readily produced that compound when gently heated. When they were cautiously heated between two watch-glasses, a portion of the substance sublimed in colourless needles. When this acid was heated with an insufficient quantity of water to dissolve it, it melted and recrystallized on cooling. These properties agree with those of nitrosalicylic acid. In order to confirm this hypothesis, the following salts were prepared.

On saturating a solution of the acid with carbonate of baryta, the baryta salt was obtained in yellow crystals. From their solution ammonia threw down another yellow-coloured baryta salt. A solution of the acid likewise produced a crystallized lead

salt. The ammoniacal salt was obtained in orange-coloured needles by saturating the acid with ammonia and crystallizing *in vacuo*. By double decomposition with the ammoniacal salt I prepared the silver combination, which, like all the others, agreed in its properties with Marchand's description of nitrosalicylic acid salts. When subjected to analysis, 0·1695 grm. of the silver salt gave

0·0630 grm. of silver, equal to 37·17 per cent.,

the quantity of silver in nitrosalicylate of silver being 37·24 per cent. When datiscine was allowed to stand in contact with dilute nitric acid in the cold, it gradually dissolved, and the liquid assumed a yellow colour. The solution, when left to evaporate *in vacuo*, was found to contain a mixture of oxalic and nitropicric acids.

Action of Potash on Datiscine and Datiscetine.—It was stated in a previous part of this paper that datiscine and datiscetine dissolve in solutions of caustic alkalies without decomposition, and that datiscine, when boiled for some time, is decomposed with formation of datiscetine. It only remained therefore to try the action of fused hydrate of potash. Datiscetine, when added in small successive portions to fused hydrate of potash, assumed a deep orange colour, and then dissolved with evolution of hydrogen gas. When the disengagement of hydrogen ceased, the mass was dissolved in water and supersaturated with hydrochloric acid. A partly crystalline resinous substance separated, which, by sublimation, yielded perfectly colourless long crystals, closely resembling benzoic acid. Their solution in water assumed, on the addition of perchloride of iron, that deep violet tint which disappears on the addition of hydrochloric acid, and is characteristic of salicylic acid.

Action of Chromic Acid.—Datiscetine was likewise distilled with bichromate of potash and sulphuric acid; the liquid which came over did not contain oily drops, but had the smell of salicylous acid, and formed with persalts of iron a purple-coloured solution.

A trace of salicylous acid appeared therefore to have been produced.

It follows therefore, I think, from the experiment already detailed, that datiscine, like salicine, phloridzine, &c., is a glucoside, and that it approaches nearer to salicine than any other glucoside, with the exception of populine, yet known. In fact I am not aware of any glucoside, with the exception of salicine and populine, which, when treated with nitric acid, yields nitrosalicylic or even nitropicric acid. Phloridzine and phloretine, for instance, when treated with nitric acid, are stated by different experimenters to yield only oxalic acid. I repeated the experiment with phloretine, and obtained much oxalic acid, while the residual liquor yielded not a trace of chloropicrine when treated

with hypochlorite of lime, and consequently contained no nitropicric acid. Quercitrine, when likewise treated with nitric acid, was also found to yield, as Rigaud states, only oxalic acid. I had no opportunity of trying esculetine, but it is stated by those who have investigated it to yield only oxalic acid.

I will conclude this account of datiscine by proposing the following practical application. As is well known, the colouring matter of madder when boiled with dilute sulphuric acid is changed into sugar and garancine, a new dye-stuff, which for many purposes is found superior to that originally present in the madder.

Within the last twelve months, Mr. Lieshing, by treating the colouring matters in weld and quercitron bark with dilute sulphuric acid, has resolved them into new colouring matters, which are but slightly soluble in water, and are found nearly three times more powerful as dye-stuffs than the original colouring matters from which they had been produced. As datiscine, when boiled with dilute sulphuric acid, undergoes a perfectly similar transformation, being resolved into sugar and datiscetine, which has a much higher colouring power than the datiscine which has produced it, I have not the least doubt that silk-dyers, who may hereafter employ solutions of *Datisca cannabina*, will find it highly advantageous to convert their datiscine into datiscetine by boiling it with dilute sulphuric acid; as the process is an extremely simple one, and as the datiscetine, from its sparing solubility in water, can be very readily obtained in a state of comparative purity.

Ptychotis Ajowan.

The *Ptychotis Ajowan* is an umbelliferous plant, well known in India for its aromatic and carminative properties. Its seeds, which very much resemble in appearance those of the caraway, only being much smaller, have a very agreeable odour, resembling oil of thyme.

On distilling these seeds repeatedly with water, the essential oil is very easily obtained, amounting to between five and six per cent. of the weight of the seeds. This oil has a light brown colour, and possesses an agreeable aromatic odour. Its specific gravity is 0·896 at 12° C.; and upon leaving the oil for some time in an open dish to spontaneous evaporation, the temperature at the time being comparatively low, large beautiful crystals were deposited, which on examination were found to be identical with the stearopten brought from India by the late Dr. Stocks, and described by me in a short notice published in the number of the "Pharmaceutical Journal" for December 1854. When the crude oil is submitted to distillation, it begins to boil at 160° C., the thermometer rising rapidly to 174° C. The thermometer then rises to 220° C., and the oil which comes over at this temperature

crystallizes on cooling. The residue, which does not immediately crystallize, on remaining at rest for some time, solidifies into a crystalline mass, the crystals having precisely the same form as those obtained by spontaneous evaporation, and amounting, in weight, to from one-third to one-fourth of the crude oil. As it seemed probable from these experiments, therefore, that Ptychotis oil, like many other essential oils, is a mixture of a liquid hydrocarbon and of a less volatile oxygenated stearopten, I proceeded to separate these compounds.

The Hydrocarbon.—The more volatile portion of the oil was redistilled, that part of it which boiled at 176° C. being separately collected. After having been dried with chloride of calcium, it was distilled over caustic potash. It was then repeatedly treated with sodium, and again cautiously rectified. The hydrocarbon thus obtained was perfectly colourless, refracted light strongly, and had a pungent, aromatic odour, quite dissimilar, however, from that of oil of thyme. Its boiling-point was found to be 172° C., a thermometer being placed in the vapour, and its specific gravity 0·854 at 12° C. Analysis shows that it is isomeric with oil of turpentine.

	Required.		Found.	
			I.	II.
C_{10} =	60	88·23	88·31	88·15
H_8 =	8	11·77	11·59	11·49
	68	100·00		

When the oil was treated with hydrochloric acid, no crystalline compound was obtained, but a brown mobile liquid, having an agreeable smell similar to the oil itself.

The Stearopten.—I have already mentioned that the portion remaining in the retort from the distillation of the crude oil solidified on cooling into a crystalline mass. When cautiously rectified it began to boil at 218° C., the thermometer, towards the latter part of the distillation, rising to 225° C., and even higher. The greater portion, however, came over at about 222° C. The first portion which came over was quite colourless, and had a mild aromatic smell, but the subsequent portions had a more pungent odour, and a yellowish colour. The more volatile, and by far the larger portion of the distillate, crystallized on cooling, especially when agitated, the crystals assuming a rhombohedral form. When it was kept quite quiet, however, it remained liquid for several days, but on being plunged into a freezing mixture it immediately solidified. The less volatile and more coloured portion of the distillate could not be made to crystallize, even when kept in a mixture of snow and salt. The form of the crystals, obtained by the solidification of the distilled stearopten, appeared at first

sight to differ from that of the stearopten from India given me by Dr. Stocks; but, upon these crystals being dissolved in the hydrocarbon of the oil, they were obtained in forms precisely similar to those of the Indian stearopten. This was also the case when either the crude or the distilled crystals were deposited from their solutions in alcohol or ether.

The following are the results of the analyses of the stearopten obtained from different sources.

A. Stearopten from India.* B. Stearopten obtained by the spontaneous evaporation of the oil. C. Distilled stearopten recrystallized from the oil.

	Required.		Found. A.			B.	C.	
C_{10} =	60	80·00	79·53	79·38	79·34	79·50	80·36	80·33
H_7 =	7	9·33	9·43	9·19	9·19	9·06	9·09	9·38
O =	8	10·67	—	—	—	—		
	75	100·00						

D. Distilled stearopten not recrystallized out of the oil. E. The same crystals recrystallized out of ether and pressed between folds of blotting-paper. F. The last (now crystallizable) part of the distillation.

	D.		E.		F.	
C =	78·58	78·26	78·84	78·90	76·71	76·92
H =	9·09	9·06	9·09	9·20	9·48	9·25

It will be seen, by the above analyses, that, during distillation, the stearopten undergoes partial decomposition, the amount of carbon being thus decreased.

The analyses D. and E. were evidently made with an impure substance, but the analysis F. agrees in a surprising manner with the numbers calculated from the formula $C_{15}H_{11}O_2$, which requires C 76·92 per cent. and 9·40 H.

I do not, however, wish it to be supposed that the formula given above, or the double of it, viz., $C_{30}H_{22}O_4$, is the true formula for that substance; nevertheless I may observe that it bears a very simple relation to the formula of the stearopten itself. The one may be regarded as

$$3C_{10}H_6 + 4HO$$

and the other

$$3C_{10}H_6 + 3HO,$$

that is, as two different hydrates of the same hypothetical hydro-

* In the December Number of the "Pharmaceutical Journal" for 1854, I published an analysis of the stearopten made from a small portion of the substance given me by the late Dr. Stocks. This I have subsequently found to be inaccurate, and the analyses given above are substituted in its stead.

carbon $C_{10}H_6$, or $C_{20}H_{12}$, which perhaps might have been obtained by distilling the stearopten with anhydrous phosphoric acid.

All experiments made with a view of determining the basic or acid properties of the stearopten, gave negative results. When an alcoholic solution of the crystals was mixed with one of acetate of lead, no precipitate was formed, and the same was the case with nitrate and ammonio-nitrate of silver. The crystals of the stearopten dissolve when gently warmed in oil of vitriol, heat being evolved, and a purple colour produced. On standing, the whole solidified, and the mass thus obtained was very soluble in water, yielding a colourless solution, with drops of a red oily liquid floating in it, produced probably by the action of the sulphuric acid on some of the hydrocarbon adhering to the stearopten. When dissolved in a small quantity of hot water, the copulated acid was deposited, on the cooling of the solution, in fine, colourless, scaly crystals. I regret that the small quantity of the substance at my disposal prevented me from determining the equivalent of the stearopten by means of the acid or one of its salts. I obtained both the baryta and the lead salt in a crystallized state by neutralizing the solutions of the acid with the carbonates of those bases. Their analysis, however, gave irregular results, as, owing to the smallness of their quantity, I could not prepare them in a state of perfect purity. In the former notice of the stearopten, already mentioned, it was stated that by long continued digestion with concentrated nitric acid, the stearopten was dissolved, and a colourless crystalline acid produced. This acid is neither oxalic acid, nor, apparently, any of the nitrogenated acids. At least, when warmed with hypochlorite of lime, it gives off no chloropicrine. I suspect, therefore, that it will be found to be a new acid, the examination of which I hope ere long to lay before the Society. From the physical properties and the elementary composition of the stearopten of the *Ptychotis Ajowan*, it struck me that it was very similar to, if not identical with, the solid portion of oil of thyme, described by Lallemand in his recent papers on that substance.* This idea induced me to distil the stearopten dissolved in oil of vitriol with an excess of peroxide of manganese. As anticipated, besides formic acid, there came over yellow drops which solidified on cooling, forming large crystals, having a peculiar odour, somewhat resembling iodine or kinone, and agreeing in every respect with the substance described by Lallemand as thymol.

Before Lallemand has published his experiments in detail, which are now only known from the two notes in the "Comptes Rendus," I do not think it possible to decide with perfect certainty whether thymol and the stearopten of the *Ptychotis* are really identical substances, and even then, perhaps, it will be

* Compt. Rend. de l'Acad. xxxvii., 498, and xxxviii., 1022.

found necessary to make more complete experiments with the stearopten of the *Ptychotis*. The hypothesis of their identity, however, appears to me highly probable from the great similarity existing in the most important properties of those substances. I may add, that I agree with Gerhardt* in considering the crystallizable substance obtained by Arppe† from the essential oil of the Horse-mint (*Monarda punctata, huile de monarde*), to be identical with Lallemand's thymol and Doveri's‡ less volatile portion of the oil of thyme.

All these substances gave nearly the same numerical results when subjected to analysis.

Doveri observed two boiling-points, one between 175° and 180° C., and the other between 230° and 235° C.

Lallemand found the boiling-point of his thymène to be 165° C., and obtained a liquid hydrochloric acid compound.

Arppe's crystallizable substance from the horse-mint oil was found to melt at 48° C., to solidify at 38° C., and to boil at 224° C.

The crystals were rhombohedral, having one angle of 97° 30′ and another of 82° 30′.

The Ptychotis oil, according to my experiments, contains a hydrocarbon boiling at 172°, and forming a liquid hydrochloric acid compound, and a crystallizable substance melting at 44° C., and boiling at about 222° C. Two properties, however, I observed different from those given by Lallemand, viz., that the stearopten of the *Ptychotis* is precipitated (in a liquid state) from its alcoholic solutions by water, and that potash does not dissolve it, but merely causes it to assume the liquid state.

From the results of these experiments, therefore, I think we may confidently infer that the stearopten of the Ptychotis oil, and the crystallizable oxygenated portion of oil of thyme, examined by Lallemand, if not identical, as I apprehend they are, are certainly extremely similar bodies.

Gum of the Gardenia lucida, Roxb. (*the Decamalee Gum of Scinde*).

The specimen of this gum on which I operated was evidently very old. It formed a hard, dry mass, of a dark brown colour, with numerous patches of greenish-yellow matter disseminated through it. It had but a faint odour, unless freshly fractured or gently heated, when it smelt like the urine of the cat. A comparatively recent specimen of this gum, which I saw in the hands of the late Dr. Stocks, had nearly the consistence of candied

* Traité de Chimie Organique, iii, 610.
† Ann. Ch. Pharm. lviii, 41; Chem. Gaz., December 1846.
‡ Ann. Ch. Phys. [3] xx, 174.

honey, and an exceedingly offensive odour. Dr. Stocks informed me that the recent gum was employed as a dressing for wounds, as it kept off the flies.

The resin was digested in strong spirits of wine till a saturated solution was obtained. This, on cooling, immediately deposited some yellow amorphous flocks. These were separated by filtration, and the clear liquid slowly evaporated *in vacuo*. On standing a few days, it deposited slender golden-yellow crystals, about half an inch in length. The crystals had considerable lustre, and were very brittle. To this crystalline substance I propose giving the provisional name of *Gardenine*.

Gardenine is nearly insoluble both in cold and hot water. It dissolves pretty readily in alcohol, but much less easily in ether, yielding bright yellow solutions, out of which it crystallizes on cooling. Alkalies, such as ammonia, do not appear to increase its solubility. It is slightly soluble in hot hydrochloric acid. Strong oil of vitriol dissolves gardenine in the cold with the production of a beautiful dark red colour. On adding water to this solution, the gardenine is precipitated apparently unchanged. Its alcoholic solutions give no precipitates with ammonio-nitrate of silver, or with basic acetate of lead. When gardenine is digested with concentrated nitric acid, it is rapidly decomposed, nitropicric acid, but apparently no oxalic acid, being produced.

Unfortunately, from the very small quantity of resin at my disposal, I was unable to prepare a sufficient amount of the gardenine, either to subject it to analysis, or to examine it more particularly. Dr. Royle has, however, already commissioned a large quantity of the resin from India, which I trust will ere long enable me to complete its examination.

Gardenine appears to belong to the tolerably numerous class of indifferent crystallizable resins, of which it is certainly one of the most beautiful.

Notes on *Datisca cannabina*, *Ajowan*, and *Decamalee Gum*, received from Dr. Royle, March 12, 1856.

Ikl-beer, the stems and roots of *Datisca cannabina*.—"*Datisca* is found both in the Old and New World, existing in the latter in Pennsylvania. *D. cannabina*, so named from its great resemblance to the Hemp-plant, extends from the south of Europe and Asia Minor through Iberia to the valleys of the Himalaya. I have obtained it from Cashmere and Kunawm, and found it at the foot of the Choor and Kedarkanta mountains. It spreads also to Nepal; *D. nepalensis*, Don, being the same species."—Royle, *Himal. Bot.* p. 340.

The *Ikl-beer* is much esteemed in the Punjab for dyeing silk of a yellow colour. It is probable that some of the silk scarves of a

lemon-yellow colour, which were much admired by artists for the delicacy of their colour, had been dyed by this substance, as it is there esteemed for dyeing silk of this colour.

Ajwain.—"The remaining Umbelliferæ, which are known in India, are those found only in a cultivated state; but this from so remote a period as to have become perfectly naturalized, and known to the natives, as well as to have names given to them in the languages of different parts of the country; some also have not as yet been found in other parts of the world;"—"as *Ptychotis Ajowan*, known everywhere by the name *Ajwain*, slightly varied in different districts."—"In addition to these, *Ptychotis sylvestris*, nob., called *arub ajwain*, is used as a carminative by the natives." —Royle, *Himalaya Bot.* p. 229.

"Dr. Roxburgh, in describing *Ligusticum Ajowan*, states, he cannot conceive that this famous Indian plant, aromatic in smell, pungent in taste, used both by natives and Europeans for culinary and medicinal purposes, can be unknown to European botanists. To *Ajwain* Persian authors assign *nankhwah* as the Arabic name. This is the Nankhwah of Avicenna, written *nanachua* and *nanachue* in the marginal translation of Ammi, in the Latin edition of his works; which names are quoted under Ammi by Mathiolus, in his Commentaries on Dioscorides. But in Persian works on Materia Medica, Aammi is also given as the Greek synonym of *nankhwah*, that is, of *Ajwain*, which Dr. Roxburgh justly supposed could not be unknown to Europeans. This plant has been referred by M. De Candolle to the genus *Ptyhcotis*, which brings it near *P. copticum*, called at one time *Ammi copticum:* the Ammi itself is called *Cuminum Æthiopicum* and *regium;* the latter name is translated by Kumoon Mullookee, and is given as a synonym of *nankhwah* in Persian authors."—*L. c.* p. 230. It is probable therefore that this Indian species of *Ptychotis* has long been employed as the Aammi of the Greeks.

Decamalee.—"This is the gum of the *Gardenia lucida.* It exudes in amber-coloured transparent drops, at the ends of the young shoots, and from thence is collected. It is most useful in preventing vermin from breeding in wounds. It is brought to Bombay from the interior."—*Bombay List of Articles for Exhibition of* 1851, p. 30.

Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, together with remarks upon the Conjugate Sulpho-acids.

By George B. Buckton, Esq., F.L.S., F.C.S., and A. W. Hofmann, L.L.D., Ph.D., F.R.S., &c.

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Ever since the experiments of Dumas, Malaguti, and Leblanc on the one hand, and those of Kolbe and Frankland on the other, have established the identity of the hydrocyanic ethers with the nitriles, it has been a favourite problem with chemists to reproduce the alcohols from these bodies, the solution of which would afford a passage from an acid $C_{2n}H_{2n}O_4$, to an alcohol $C_{2n-2}H_{2n}O_2$.

We have been likewise engaged with this question. The deportment of hydrocyanic acid (formonitrile) under the influence of concentrated sulphuric acid, which, as is well known, gives rise to an evolution of carbonic oxide, suggested an examination of the other nitriles in a similar direction. There appeared to be a chance of producing in this manner from a nitrile, the sulpho-vinic acid of an alcohol containing two equivalents of carbon less than the nitrile. Acetonitrile, for instance, might have been thus converted either into sulphate of methylammonium or into sulpho-methylate of ammonium.

$$\underbrace{HCN_2}_{\text{Hydrocyanic acid.}} + 2HO + H_2S_2O_8 = 2CO + \underbrace{\left\{\begin{matrix}H\\NH_4\end{matrix}\right\}S_2O_8}_{\text{Bisulphate of ammonium.}}$$

$$\underbrace{C_2H_3C_2N}_{\text{Acetonitrile, or Cyanide of methyl.}} + 2HO + H_2S_2O_8 = 2CO + \underbrace{\left\{N\begin{pmatrix}H\\H_3\\C_2H_3\end{pmatrix}\right\}S_2O_8}_{\text{Bisulphate of methylammonium.}}$$

$$\text{or} \quad = 2CO + \underbrace{\left\{\begin{matrix}NH_4\\C_2H_3\end{matrix}\right\}S_2O_8}_{\text{Methylosulphate of ammonium.}}.$$

Experiment has not corroborated either of these anticipations. This reaction gives rise to the formation of a remarkable conjugate sulpho-acid, which may be considered as the type of a most extensive class of analogous compounds, some isolated terms of which have been met with already in previous investigations.

Before, however, detailing the conditions under which these

new bodies are formed, it may not be unacceptable to make a few statements regarding the most efficient method of procuring the nitrile of the methyl-series in quantity and in a state of purity.

Preparation of Acetonitrile.

The preparation of cyanide of methyl (acetonitrile), by decomposing sulphomethylate of potassium with cyanide of potassium, is unsatisfactory, both as to quantity and quality of the product obtained. The presence of a minute amount of moisture in the materials employed gives rise to a number of secondary products, the chief of which are cyanide and carbonate of ammonium, and a gas possessing a highly offensive odour, which imparts to the distillate a smell not at all due to the nitrile itself. By far the most advantageous method of preparing acetonitrile consists in acting upon acetamide with anhydrous phosphoric acid, as proposed by M. Dumas.

Acetic ether is not immediately soluble in a moderate quantity of aqueous ammonia; but after five or six hours' contact, the layers at first formed disappear, and the liquid becomes homogeneous.

If distillation be now at once commenced, scarcely a trace of acetamide will be obtained. The change, on the other hand, is complete if the mixture be exposed for some hours to a temperature of 120° or 130° C.

We have employed in this operation a wrought-iron cylinder, similar to that used by Dr. Frankland in his researches, which had been constructed for us by Mr. James Nasmyth, who never fails most kindly and liberally to lend the extraordinary resources of his celebrated establishment for scientific purposes. Equal volumes of acetic ether and concentrated ammonia were introduced into the boiler, the brass valve of which was protected from corrosion by a steel screw and leaden washer. After six hours' digestion, the acetamide was separated by distillation with the thermometer from the alcohol formed, that part only being reserved as anhydrous which had passed over above 200°. When acetamide is intimately mixed with about an equal volume of anhydrous phosphoric acid in a retort, a powerful action commences immediately, and the nitrile passes over colourless, but contaminated with acetic and hydrocyanic acids. Towards the end of the operation, it is necessary to use a strong heat to drive off the last portions. The distillate is now agitated with just sufficient aqueous potash to neutralize the acids, when the nitrile floats on the surface, and may be removed for rectification over a fresh quantity of phosphoric acid, to render it perfectly anhydrous. Pure acetonitrile possesses an ethereal odour, faintly recalling that of cyanogen; its aromatic taste is pungent, but not disagreeable.

We observed the boiling-point 77°—78°, which coincides with that observed by Dumas. It does not appear to have been previously noticed, that acetonitrile burns with a luminous flame, the edges of which are beautifully tinged with peach-blossom colour. The flame and odour of acetonitrile unmistakeably bespeak the cyanic relations of this compound.

Action of Sulphuric Acid on Acetonitrile.

This body, when mixed with its own volume of fuming sulphuric acid, gives rise to a very energetic reaction, a considerable amount of heat being evolved, which causes much of the nitrile to volatilize and thus escape decomposition. In order to avoid this, the operation is best conducted in a retort surrounded with cold water, when a perfect mixture can be effected, scarcely a change of colour becoming perceptible. On application of heat, the mixture intumesces powerfully with copious evolution of a gas which, on examination over mercury, proves to be carbonic acid, without a trace of carbonic oxide; at the same time strong acetic acid passes into the receiver. If the temperature be kept up by the gas-flame until the effervescence almost entirely ceases, the mass when cold forms a brown, tough, and transparent solid, readily soluble in water and in alcohol. The aqueous solution, boiled with an excess of carbonate of barium, is then passed through a hot-water filter, when a magnificent salt is deposited, in the form of brilliant colourless rectangular plates which, when gathered in mass, exhibit a nacreous lustre. This salt is remarkably stable. It loses no weight at 100° C., but gives off water of crystallization somewhat below 150°. At a temperature of 220° the substance still remains unaltered, but when heated beyond this point, it begins to turn yellow, and disengages water, sulphurous acid and carbonic oxide, whilst sulphur sublimes. When strongly heated, it becomes incandescent, leaving a residue of sulphate and sulphite of barium. The new salt may be crystallized unchanged from hydrochloric acid, and may be boiled for hours with concentrated nitric acid, without formation of sulphate of barium. It is quite insoluble in alcohol.

Action of Sulphuric Acid upon Acetamide.

As acetamide differs from acetonitrile only in containing two additional equivalents of water, this compound, when heated with fuming sulphuric acid, undergoes a perfectly analogous transformation.

From the comparative facility of its preparation, acetamide offers peculiar advantages for procuring the new substance in large quantity. The chief difficulty which presents itself consists in

operating with the right proportions of acid and amide. Distillation of equal volumes of dry acetamide and ordinary Nordhausen acid, for instance, gives scarcely a trace of anything but acetic acid and sulphate of ammonia. The most efficient proportions we found to be two volumes of amide to three volumes of acid. The distillation should be pushed very far, in fact until the product of distillation is accompanied by sulphurous acid. The solution of the solid residue may at once be saturated with carbonate of barium; it will be found, however, more economical to treat the liquid with finely-powdered Carrara marble until the free acid is neutralized, and to reserve the pure carbonate of barium, which is so difficult to wash thoroughly, merely for decomposing the sulphate of ammonium towards the end of the process. The liquid must be boiled with excess of the carbonate until a filtered sample ceases to give an insoluble precipitate with chloride of barium. The liquid thus obtained contains now in solution chiefly two ammonium-salts, one of which is scarcely crystallizable, whilst the other forms large and regular rhombic crystals, sometimes an inch in diameter. In addition to these ammonium-salts, a certain quantity of barium- and even calcium-salts are present, which it is necessary to decompose by carbonate of ammonium in excess before an attempt is made to effect a separation of the two salts.

On adding a saturated solution of either chloride or acetate of barium to a moderately strong solution of the crystallized ammonium-salt, the liquid becomes, in the course of a few minutes, nearly solid from the deposition of a mass of crystals of a barium-compound, which may be collected on a filter and well washed with cold water to free it from the chloride of ammonium and excess of the precipitant.

One recrystallization from boiling water furnishes this salt in a state of purity. It in no manner differs from the barium-salt previously described as procured from acetonitrile. The identity is moreover proved by analysis.

From the analytical data we calculate for the anhydrous salt the formula

$$C\,H\,Ba\,S_2\,O_6,$$

but considerations which we shall develope hereafter, especially the production of similar compounds in analogous series, induce us to double this expression, and to represent the new barium-salt by the formula,

$$C_2\,(H_2\,Ba_2)\,S_4\,O_{12}.$$

The salt, as already stated, retains water of crystallization at 100° C. In two determinations this water was found to amount to 2 equivalents.

The formula of the crystallized salt is therefore

$$C_2(H_2\,Ba_2)\,S_4\,O_{12}+4aq.$$

We propose for this substance the name *disulphometholate of barium*, and for the acid the term *disulphometholic acid*, without wishing, however, to express by this term any particular view regarding the actual arrangement of the constituent molecules in the substance.

If the formula above given be correct, disulphometholate of barium is the salt of a bibasic acid, the composition of which would be represented by the expression

$$C_2 H_4 S_4 O_{12},$$

furnishing salts of the general formula,

Acid salt . . . $C_2 (H_3 M) S_4 O_{12}$
and Neutral salt . . $C_2 (H_2 M_2) S_4 O_{12}$.

The barium-salt which has been described belongs to the second class.

We have not yet succeeded in preparing any acid salts. Disulphometholate of barium crystallizes unchanged from a hydrochloric acid solution.

Disulphometholic Acid.—To prepare this acid, the barium-salt is precipitated by a small excess of sulphuric acid, which is again removed by means of oxide of lead. Hydrosulphuric acid is then passed through the liquid, which thus becomes strongly acid. It may be concentrated to a syrup without decomposition, and even carefully heated until white fumes appear. On cooling the liquid thus concentrated under the receiver of the air-pump, a crystalline mass of fine radiated needles is produced, exceedingly soluble in water and very deliquescent. They have a pure acid taste, with somewhat the flavour of tartaric acid. The attraction of this acid for water is so great, that we have failed in obtaining it in a solid condition by evaporation over sulphuric acid.

It is not changed by boiling with nitric acid, and chlorine gas passed through the aqueous solution does not liberate sulphuric acid.

The corresponding salts are readily obtained by digesting the oxides or the carbonates of the various metals with solution of the acid. The barium-salt is immediately precipitated by adding chloride of barium to this solution. The salts are all soluble in water, but insoluble in alcohol.

Disulphometholate of Silver crystallizes either in tufts of flat needles, or in broad tables of considerable size. It is produced when the aqueous solution of the acid is neutralized with carbonate or oxide of silver. We had hoped to obtain crystals of sufficient regularity for measurement of the angles; but although they may be easily produced of sufficient size, the edges are mostly rounded and imperfect.

It bears a temperature of 150° C without decomposition, but

blackens and froths when strongly heated, yielding sulphur, sulphurous acid, and metallic silver. It is insoluble in absolute alcohol, but may be crystallized from spirits of wine.

This salt contains

$$C_2(H_2Ag_2)S_4O_{12}.$$

Disulphometholate of Ammonium.—The formation of this substance has been already described. It is sparingly soluble in cold, but very soluble in hot water; from which it is again deposited in colourless crystals, often an inch in length. They are anhydrous, decrepitate when heated, and bear a temperature of 190° without being changed.

Through the kindness of Mr. Charles Brooke, we are enabled to state that the crystals of this salt belong to the oblique prismatic system, which is in fact nothing more than a hemihedral form of the right prismatic system.

When submitted to analysis, this salt gave numbers corresponding with the formula

$$C_2[H_2(NH_4)_2]S_4O_{12}.$$

Disulphometholate of Potassium is most readily obtained by adding the crystallized barium-salt by degrees to a boiling solution of carbonate of potassium, avoiding an excess of the former. After filtration, the new substance separates easily from excess of alkali in fine shining needles or brilliant grains, according to the rapid or slow precipitation from its solution. It is not very soluble in cold water, one part requiring fourteen parts of water at 22° C for solution.

Disulphometholate of Zinc.—When metallic zinc is heated with an aqueous solution of the acid, hydrogen gas is liberated, and on concentration, a syrup is formed which crystallizes with great difficulty. Alcohol does not precipitate this salt from its solution.

Disulphometholate of Lead forms small square nacreous plates not unlike those of the barium-compound. It is very soluble in water.

Disulphometholate of Copper is produced by careful precipitation of the barium-salt by sulphate of copper. It yields radiated needles or small prisms of a green colour. They are insoluble in absolute alcohol, but soluble in spirits of wine.

We have not succeeded in preparing the ethers of this acid. We anticipated that they would be formed by bringing together iodide of ethyl and disulphometholate of silver. A strong solution of the silver-salt reacts at once on the iodide without application of heat. Iodide of silver is precipitated; but the ether which is formed splits immediately into disulphometholic acid and alcohol, according to the equation

$$C_2(H_2Ag_2)S_4O_{12}+2C_4H_5I+4HO=2AgI+2C_4H_6O_2+C_2H_4S_4O_{12}.$$

Examination of the mother-liquor of Disulphometholate of Ammonium.

Sulphacetate of Ammonium and Sulphacetate of Barium.

It has been already noticed that another salt is present in the mother-liquid obtained during the purification of disulphometholate of ammonium. To procure this substance in a state of purity, the mother-liquid was concentrated, and the crystals of the disulphometholate removed from the thick syrup as completely as possible.

After a moderate addition of cold water, the liquid was mixed with an excess of chloride of barium, and the whole allowed to stand for five or six minutes, when it was filtered, and the filtrate set apart for twenty-four hours. At the expiration of this time, a copious granular precipitate had formed which was well washed with cold water, and then recrystallized from boiling water, in which, when once deposited, it proved to be very little soluble.

This substance differs both in its crystalline form and in its reactions from the disulphometholate. When strongly heated, it turns black and burns away like tinder. The residuary mass, moistened with hydrochloric acid, evolves hydrosulphuric and sulphurous acid, according to the time of ignition.

The percentage of barium, obtained in the analysis of this salt, agrees well with the amount required by the formula, $C_4(H_2Ba_2)S_2O_{10}$, of sulphacetate of barium.

The quantity of sulphacetate of ammonium produced, mainly depends upon the degree of heat maintained during the reaction of sulphuric acid upon acetamide or acetonitrile. If the mixture be made gradually and cooled after each addition of acid, the elimination of carbonic acid may be entirely prevented, and the chief product is then sulphacetic acid. On the other hand, if the heat be urged as far as is practicable, disulphometholic acid takes the place of the sulphacetic, carbonic acid being evolved at the same time.

Two phases may therefore be traced in the reaction. In the first, nascent acetic acid simply combines with the elements of two equivalents of anhydrous sulphuric acid. In the second phase, the acetic molecule undergoes a more thorough transformation, splitting, as it does, into carbonic acid and marsh-gas, the latter of which combines with the elements of four equivalents of anhydrous sulphuric acid.

The new acid may also be regarded as sulphacetic acid, which, losing carbonic acid, has assimilated an equal number of equivalents of anhydrous sulphuric acid.

The two stages in the action of sulphuric acid on acetonitrile may be represented by the following equations:—

$$\underbrace{C_4H_3N}_{\text{Acetonitrile.}} + 2HO + 2H_2S_2O_8 = \underbrace{C_4H_4S_2O_{10}}_{\text{Sulphacetic Acid.}} + \left.\begin{matrix} H \\ NH_4 \end{matrix}\right\} S_2O_8$$

$$\underbrace{C_4H_3N}_{\text{Acetonitrile.}} + 3H_2S_2O_8 = \underbrace{C_2H_4S_4O_{12}}_{\text{Disulphometholic acid.}} + \left.\begin{matrix} H \\ NH_4 \end{matrix}\right\} S_2O_8 + 2CO_2.$$

Acetamide containing but two equivalents of water more than acetonitrile, the production of sulphacetic acid and disulphometholic acid from this substance is intelligible by means of the same equations.

The action then of bases and of acids upon acetic acid presents a remarkable analogy. Under the influence of both agents, we may assume, it splits into marsh-gas and carbonic acid; in the first case, it is the carbonic acid which is fixed by the alkali, whilst in the latter the marsh-gas remains in combination with the acid.

The possibility of assuming the existence of marsh-gas in disulphometholic acid, suggested the idea of endeavouring to combine marsh-gas directly with sulphuric acid. The dry gas obtained by the distillation of acetate of soda with potash-lime was passed into a receiver charged for this purpose with anhydrous sulphuric acid, but we could not detect any combination of the two bodies, either at the ordinary temperature or when the receiver was heated to 100° C. The sulphuric acid, after treatment with water and carbonate of barium, furnished no soluble salt whatever.

Although we have thus been unable to convert marsh-gas into disulphometholic acid, we have found that this acid may be readily transformed into marsh-gas. When heated with hydrate of baryta the salts of the acid yield marsh-gas, together with sulphate and sulphite of barium. A method is thus indicated by which probably all the hydrocarbons, $C_{n2-2}H_{n2}$, may be prepared from the corresponding sulpho-acids.*

The simplicity of relation which exists between sulphacetic and disulphometholic acid, left no doubt in our mind regarding the convertibility of the former into the latter. We have established this fact moreover experimentally. Sulphacetic acid, prepared by the action of anhydrous sulphuric acid upon glacial acetic acid, furnished without difficulty disulphometholic acid, when again treated with sulphuric acid. A similar observation had in fact been made already by M. Melsens. This chemist, in his researches upon the sulphacetates, appears in some sort to have anticipated

* We are unable to corroborate M. Aimée's remarks, that marsh-gas is decomposed by sulphuric acid into water, carbon, and sulphurous acid. The acid remains colourless, and the gas after the process exhibits its usual properties unmodified.

the existence of the disulphometholates. He remarks that he once found in the mother-liquor, obtained from the preparation of sulphacetate of silver, a crystalline salt the composition of which he represents by the formula

$$C_2H_2Ag_2S_4O_{12}.$$

It is evident that this was nothing but the disulphometholate of silver, but M. Melsens does not appear to have investigated the subject further, or to have connected the appearance of this salt with the evolution of carbonic acid gas, which he likewise found among the secondary products of the action of sulphuric acid upon acetic acid.

The chemical character of disulphometholic acid is so marked and the reaction which produces it so simple and definite, that there could be no doubt regarding the existence of numerous corresponding terms in homologous and even in analogous series of substances. In fact disulphometholic acid may be considered as the type of a very numerous class of bodies of similar composition, some of which are actually known, while a great many remain to be discovered.

We have ourselves traced the formation of the homologues and analogues of disulphometholic acid in several higher series of bodies, but we have been satisfied in establishing the existence of these substances, without entering into a detailed study of their properties.

Ethyl-Series.

Preparation of Propionitrile.

The formation of cyanide of ethyl (propionitrile) by means of cyanide and sulphovinate of potassium, has all the disadvantages above enumerated in the case of cyanide of methyl. A large quantity of an inflammable gas of a highly offensive odour is disengaged, the annoyance of which may be avoided by conducting the gas from the receiver of the liquid into the cylinder of a wire gauze burner, in the air-flame of which it is perfectly consumed. In the preparation of cyanide of ethyl by means of cyanide and sulphovinate of potassium, through the intervention of unavoidable moisture, a variety of different reactions appear to proceed side by side. Together with the formation of cyanide of ethyl,

$$\underbrace{(C_4H_5,K),S_2O_8}_{\text{Sulphovinate of potassium.}} + KCy = \underbrace{C_4H_5Cy}_{\text{Cyanide of ethyl.}} + K_2S_2O_8$$

considerable quantities of carbonate of ammonium are produced, whilst an inflammable gas is largely generated, which is nothing but hydride of ethyl. This gas is not absorbed by bromine; it therefore cannot contain any ethylene. It combines with chlorine,

forming a gaseous compound, burning with a green-edged flame. This is probably the substance obtained by Drs. Kolbe and Frankland when treating ethyl with chlorine gas, isomeric with chloride of ethyl, C_4H_5Cl. When in contact with excess of chlorine it yields an oily substance, and a crystalline body having the properties and composition of sesquichloride of carbon.

It is from this fact chiefly that we infer the identity of the inflammable gas generated in the preparation of propionitrile with hydride of ethyl,

$$\underbrace{C_4H_6}_{\text{Hydride of ethyl.}} + 12Cl = \underbrace{C_4Cl_6}_{\text{Sesqui-chloride of carbon.}} + 6HCl.$$

The oily liquid observed obviously consisted of the intermediate substitution-terms.

These substances are evidently secondary products of the decomposition of cyanide of ethyl,

$$\underbrace{C_4H_5Cy}_{\text{Cyanide of ethyl.}} + 6HO = \underbrace{C_4H_5H}_{\text{Hydride of ethyl.}} + \underbrace{\left.\begin{matrix} H \\ NH_4 \end{matrix}\right\} C_2O_6}_{\text{Bicarbonate of ammonium.}}.$$

Cyanide of ammonium is likewise invariably present, prussic acid being generated by the action of water upon the cyanide of potassium, while alcohol is reproduced to a very considerable extent. Lastly, this process gives rise to a most remarkable body with a most insupportable prussic smell, the formation of which we have traced in a great variety of reactions. We have not completed the study of this compound.

The method finally adopted for obtaining propionitrile in sufficient quantity for us to experiment upon was that recommended by Dr. Williamson, viz., the digestion of cyanide of potassium with iodide of ethyl in four volumes of alcohol as a vehicle. The presence of so much alcohol, from which the cyanide cannot be separated by rectification, on account of the similarity of their boiling-points, is an evil which unfortunately involves a series of tedious processes, namely, conversion of the nitrile into propionate of potassium, by the action of caustic potassa, separation of the alcohol by distillation, preparation of propionic ether, transformation of the latter into propionamide by the action of ammonia under pressure, action of phosphoric acid upon propionamide to form the nitrile, and ultimately dehydration of the nitrile by means of anhydrous phosphoric acid.

In preparing disulphetholic acid we have almost invariably employed propionamide, on account of its easier preparation.

We have, however, established by experiment that propionitrile exhibits with sulphuric acid exactly the same deportment as propionamide. To effect the transformation of the propionamide with success, it is necessary to employ this substance in a perfectly anhydrous condition. Unless this point be properly attended to, sulphuric acid produces principally sulphate of ammonium and propionic acid; for this purpose the amide should be heated in a retort, and that portion only collected which passes over above the temperature of 210° C. Below this point the amide retains sufficient water to prevent perfect crystallization.

On mixing equal volumes of melted amide and fuming sulphuric acid, very considerable heat is disengaged; the temperature must be regularly maintained until carbonic acid ceases to be evolved and propionic acid no longer distils over. Some experiments are necessary in order to fix the quantity of acid required for the conversion of the propionamide, since commercial Nordhausen acid varies considerably in composition. If too much acid be employed, the mixture is often perfectly carbonized, whilst too little acid gives rise to the formation of either sulphopropionic or propionic acid.

If care be taken to regulate the heat so as just to keep up the liberation of carbonic acid, the amount of disulphetholic acid may be considerably increased.

The solid residue in the retort, when cold, is dissolved in water, and treated, as in the case of disulphomethollic acid, first with carbonate of barium, and subsequently with carbonate of ammonium. On evaporation the liquid thus obtained furnishes two salts, one of which is quite uncrystallizable, and must be separated from the other by washing with weak spirit. A crystalline substance remains on the filter, which, after two or three crystallizations from hot water, is the pure

Disulphetholate of Ammonium.—When deposited from an aqueous solution, this salt forms regular cubic crystals or square prisms, perfectly colourless. It is insoluble in alcohol and in ether. In its general behaviour this substance differs but little from the corresponding salt of the methyl-series, the principal feature of difference being a greater solubility and its leaving a carbonaceous residue when strongly heated.

Disulphetholate of Barium crystallizes with regularity in six-sided plates, which generally arrange themselves from centres. It is easily formed by heating a solution of the ammonium-salt with hydrate of baryta until every trace of ammonia is expelled, and then passing a current of carbonic acid through the solution to remove the excess of baryta. It is very soluble in water, and stable at a temperature of 180°, but blackens when strongly heated in close vessels, empyreumatic vapours being at the same time given off. The black residue burns with a sulphur-flame.

Disulphetholate of barium is insoluble in concentrated nitric acid, which does not decompose it. It crystallizes from the dilute acid without apparent change.

After fusion with chlorate of potassium and carbonate of sodium, the filtrate contains sulphates in solution, proving that there is more sulphur present than is required for saturating the barium of the compound. By this method the disulphetholates can be distinguished from the sulphopropionates presently to be described.

On analysis the barium-salt furnished numbers which accord with the formula

$$C_4(H_4Ba_2)S_4O_{12}.$$

A determination of the water renders it probable that the salt contains 2 equivalents of water.

As has been already stated, the disulphethylates may also be prepared from propionitrile. For this purpose three parts of the propionitrile are distilled with two parts of fuming sulphuric acid. As the action is very energetic, the mixing should be effected by degrees in a moderate-sized retort. A barium-salt was prepared the properties of which agreed in every respect with those of the compound prepared from propionamide.

Disulphetholic Acid is obtained by decomposing the lead-salt by hydrosulphuric acid. By concentration it forms a thick syrup, which ultimately solidifies into a crystalline mass. By heat it decomposes with deposition of charcoal and production of white fumes.

Disulphetholate of Silver may be obtained by a process similar to that employed in the case of the disulphometholate. It is crystalline. When dry, it bears a considerable heat without change. The solution blackens on ebullition.

Disulphetholate of Lead is very soluble in water. When evaporated over sulphuric acid, the salt yields fine prisms or minute quadrangular laminæ. When hastily evaporated it produces a tough gummy mass.

Sulphopropionic Acid.—As might have been anticipated from the results obtained in the methyl-series, disulphetholic acid is by no means the sole product of the action of sulphuric acid upon propionamide and propionitrile. The formation of this acid is preceded by that of another acid richer in carbon and poorer in sulphur, in one word, by that of sulphopropionic acid. The uncrystallizable ammonium-salt, already mentioned, is in fact the sulphopropionate of ammonium. Absolute alcohol throws it down from its solution as a thick treacly mass, with an appearance very unprepossessing to the analyst. The dilute aqueous solution was therefore boiled with carbonate of barium until entirely decomposed, and the filtered liquid concentrated in a beaker. At a particular point of the evaporation, a quantity of *sulphopropionate of*

barium appeared in small cubic grains, which caused so much "bumping" as to make it necessary to evaporate upon the water-bath.

If the concentration be arrested before the deposition of these grains, and the liquid be set aside for twenty-four hours, it yields a plentiful crop of beautiful silky crystals, arranged in spherical groups.

After another crystallization from hot water, in which the substance is moderately soluble, this salt is sufficiently pure for analysis. It was dried at 170°, and gave on analysis numbers which agree with the formula of sulphopropionate of barium,

$$C_6(H_4Ba_2)S_2O_{10}.$$

Propyl-Series.

From what has been already said, but few words are necessary on the preparation of disulphopropiolic and sulphobutyric acid. It may, however, be stated, that butyramide boils at 116°, and passes over at that temperature in drops which crystallize beautifully. It has the characteristic sweet taste of the other amides of the series, and, like them, it fumes slightly in the air when gently heated.

Three parts of butyramide produce with two parts of fuming sulphuric acid a horny mass, which, after removal of the sulphuric acid and saturation with ammonia, yields a syrup wholly uncrystallizable. The ammonium-salts were converted into barium-salts, which also possess but feeble powers of crystallization.

M. Redtenbacher has already pointed out how much the solubility in water of the barium-salts of the acids $C_{2n}H_{2n}O_4$ augments as the value of the coefficient n progressively increases. A similar increase of solubility is observed with the barium-salts of the series of conjugated acids which form the subject of this paper. The contrast between the almost insoluble disulphomethotate and the very soluble disulphopropiolate of barium is very marked.

From the extreme solubility of these salts, great difficulty was experienced in separating them completely one from the other. The method adopted was that of partial precipitation by alcohol. To solutions moderately concentrated and cold, sufficient absolute alcohol was added to produce a cloud, permanent when rapidly stirred. On allowing the liquid to stand for an hour, a quantity of a granular substance attached itself to the glass vessel, which, after solution in water and reprecipitation, was dried and decomposed by sulphuric acid.

A barium-determination in the salt led to the formula for sulphobutyrate of barium,

$$C_8(H_6Ba_2)S_2O_{10}.$$

We have not been able to procure the disulphopropiolate of barium in a state of purity. The alcoholic liquid which remains after deposition of the sulphobutyrate contains a considerable quantity of the salt, but so mixed, that we were unable more than proximately to isolate it. By continuing the process of fractional precipitation, and drying, and by analysing the different samples, the quantity of barium present in the successive specimens was found to decrease, the last and lowest number agreeing nearly with the formula of disulphopropiolate of barium,

$$C_6(H_6Ba_2)S_4O_{12}.$$

This salt is not so wholly uncrystallizable as the sulphobutyrate. By slow evaporation it furnishes very minute crystals, which under the microscope show themselves as thin pearly plates. They appear best when slowly thrown down by alcohol from the solution.

Butyl-Series.

Our experiments in this series have been entirely qualitative. We have been satisfied to establish experimentally the analogy of the reactions. These reactions, however, become less and less definite, and, owing to the still greater solubility of the new products, their separation is attended with difficulties almost insurmountable.

The researches detailed on the preceding pages are quite sufficient to establish the general character of the action of sulphuric acid upon the amides and nitriles. Nevertheless, since these experiments exclusively refer to the derivatives of several *homologous* terms of the series of *fatty* acids, it appeared desirable to extend the investigation to a nitrile of the *analogous* group of *aromatic* acids. No substance appeared to be more appropriate for such an examination than benzonitrile, or cyanide of phenyl.

Phenyl-Series.

Preparation of Benzonitrile.

M. Fehling originally obtained benzonitrile by subjecting benzoate of ammonium to repeated dry distillations, when the four equivalents of water gradually separated. The process is however objectionable, on account of the necessity of repeatedly returning by hand the sublimed salt to the volatilizing vessel. We hoped to have found a more convenient method, in submitting the same salt to the dehydrating action of chloride of zinc; but on rectifying the distillate, we obtained only one-third of the product in the form of benzonitrile, the remaining portion being

benzole. The safest, but somewhat lengthened, process for procuring benzonitrile, consists in dehydrating benzamide with anhydrous phosphoric acid, the former body having been produced by the action of carbonate of ammonium upon chloride of benzoyl, as recommended by M. Gerhardt.

Action of Sulphuric Acid upon Benzonitrile.

Sulphuric acid and benzonitrile mix with liberation of far less heat than is observable in the cases previously recounted. No gas is disengaged until the temperature is very considerably raised, when a portion of benzoic acid sublimes in the neck of the retort and carbon is deposited, while sulphurous acid is simultaneously disengaged. The action was continued for some time after the appearance of sulphurous acid, for the purpose of decomposing the sulphobenzoic acid which analogy would lead us to expect among the products of the reaction. On cooling, a semi-transparent hard mass of glassy fracture remained in the retort. The usual treatment with carbonate of barium evolved ammonia, showing the presence of a salt of that base.

Sulphobenzoate of Barium.—As the filtrate was very dark-coloured, the barium-salt was again decomposed by sulphuric acid, and then boiled with excess of oxide of lead, filtered and treated by hydrosulphuric acid. The sulphide of lead was found to carry down with it almost the whole of the colouring matter. The acid liquid was then saturated with carbonate of barium, a portion evaporated nearly to dryness and treated with hydrochloric acid, when a salt crystallized out from the mother-liquor, which, after washing with water, was again crystallized until free from hydrochloric acid.

Dried at 200°, it gave a percentage of barium which coincided with that required by the formula $C_{14}(H_5Ba)S_2O_{10}$ of the acid sulphobenzoate of barium analysed by Mitscherlich and Fehling.

It was therefore obvious that the disulphosalt, if present, was the most soluble, and to be found in the filtrate.

The remaining portion of the neutral solution of the barium salt was therefore dissolved in water, and about one-half of the solid matter precipitated by alcohol filtered off and recrystallized, the percentage of barium in which was found to correspond to the neutral sulphobenzoate of barium, $C_{14}(H_4Ba_2)S_2O_{10}$.

Disulphobenzolate of Barium.—It remained, therefore, to examine the salt last thrown down by alcohol, which, after being purified again by precipitation, gave analytical numbers characterizing the new salt, although still in a state of admixture with sulphobenzoate of barium.

The results of the analysis, leading unequivocally to the

formula $C_{12}(H_4Ba_2)S_4O_{12}$ could leave no doubt regarding the nature of the substance analysed, yet it was desirable, if possible, to prepare the new compound in a state of purity; and the question presented itself, whether it could not be more directly formed from sulphobenzolic acid, $C_{12}H_6S_2O_6$, which is so easily obtained by the action of sulphuric acid upon benzol. Success in its preparation by this means was of considerable interest, since in this case it would become highly probable that all the new bodies hitherto described in this memoir might be prepared, from the analogues of sulphobenzolic acid in their respective groups, by a simple assimilation of the elements of sulphuric acid. The method in question is in reality by far the best adapted for procuring the new acid in a state of purity. Sulphobenzolic acid obtained from the lead- or copper-salt is evaporated on the sand bath until the evolution of white fumes proves that the greater part of the water has been volatilized. It is advisable to heat the solution until a slight brown coloration indicates incipient decomposition. The acid is then introduced into a dry retort, together with an equal volume of strong Nordhausen acid, and the whole maintained at the boiling-point for two hours. The liquid is then reduced by evaporation nearly to the original bulk of the sulphobenzolic acid employed. The new acid in this stage has a very dark colour which cannot be removed by boiling with charcoal. Treatment, however, with an excess of oxide of lead, and decomposition of the filtrate by hydrosulphuric acid, furnishes a liquid which is perfectly colourless.

When this liquid is saturated with carbonate of barium and evaporated, an apparently amorphous mass is produced which, however, under the microscope is distinctly crystalline, showing minute shuttle-shaped forms generally densely grouped together. This salt is very stable. Strongly heated, however, on platinum foil, it burns with evolution of sulphurous acid.

Analysis furnished numbers leading to the formula of disulphobenzolate of barium,

$$C_{12}(H_4Ba_2)S_4O_{12}.$$

The preceding researches establish in two different groups of bodies the existence of a series of bibasic acids, containing 4 equivalents of sulphur, and which, irrespectively of any special view regarding their molecular arrangement, may be represented as formed by the association of the hydrocarbons (corresponding to marsh-gas) of the various groups with 4 equivalents of anhydrous sulphuric acid:—

Disulphometholic acid	$C_2H_44SO_3$
Disulphetholic acid	$C_4H_64SO_3$
Disulphopropiolic acid	$C_6H_84SO_3$
Disulphobenzolic acid	$C_{12}H_64SO_3$.

An acid of analogous composition exists in the naphthalin-series:—

Disulphonaphtholic acid . . . . . $C_{20}H_8 4SO_3$,

which was discovered by Berzelius, and subsequently studied by Laurent.

Many of these substances may actually be produced directly from the hydrocarbons by the action of sulphuric acid. On the other hand, chemists are well acquainted with the deportment of olefiant gas under the influence of anhydrous sulphuric acid. The crystalline compound discovered by Magnus, and described by him under the name of Sulphate of Carbyl, whatever its constitution may be, can be considered as a direct combination of olefiant gas with four equivalents of anhydrous sulphuric acid,

Sulphate of Carbyl . . . . $C_4H_4 4SO_3$.

It can scarcely be doubted that all the other hydrocarbons of the series $C_{2n}H_{2n}$, propylene, butylene, amylene, &c., will furnish homologous substances.

Sulphate of carbyl, when submitted to the action of water, assimilates two equivalents, and is converted into a bibasic acid (ethionic), $C_4H_4 4SO_3 + 2HO = C_4H_6O_2 4SO_3$, which accordingly may be viewed as an association of alcohol with four equivalents of anhydrous sulphuric acid. Terms analogous to ethionic acid are sure to be found when the study of the homologues of sulphate of carbyl shall be taken up by chemists.

The production of disulpho-compounds of perfectly similar composition, from substances belonging to such different groups of bodies as the hydrocarbons, homologous and analogous to marsh-gas, as ethylene, and as alcohol, suggested the possibility that the substances observed might be but individual examples of a far more general mode of formation. It became, in fact, probable that all organic bodies, capable of uniting with the elements of two equivalents of anhydrous sulphuric acid, might, under favourable circumstances, be induced to assimilate two additional equivalents of anhydrous sulphuric acid, and thus furnish terms belonging to the class of disulpho-compounds.

The hope of arriving at a more general interpretation of our observations induced us to institute some further inquiries, the result of which we will briefly append.

The first question which naturally suggested itself, was the examination of the deportment of the sulpho-acids derived from acetic, propionic, butyric, benzoic acid, &c., under the influence of an excess of sulphuric acid. To take acetic acid as an illustration, Is sulphacetic acid, $C_4H_4S_2O_{10} = C_4H_4O_4 2SO_3$, capable of combining with two additional equivalents of sulphuric acid in order to furnish the compound $C_4H_4S_4O_{16} = C_4H_4O_4 4SO_3$? The experiments hitherto detailed contain no evidence against this assump-

tion. It appeared to us extremely probable that sulphacetic acid, when submitted to the action of sulphuric acid, is converted into disulphacetic acid, which, losing carbonic acid, produces disulphometholic acid, the deportment of disulphacetic under the influence of heat being closely analogous with that of acetic acid,

$$\underbrace{C_4H_4O_4}_{\text{Acetic acid.}} \quad 2CO_2 = \underbrace{C_2H_4}_{\text{Marsh-gas.}}$$

$$\underbrace{C_4H_4O_4 4SO_3}_{\substack{\text{Supposed}\\ \text{disulphacetic acid.}}} - 2CO_2 = \underbrace{C_2H_4 4SO_3}_{\substack{\text{Disulphometholic}\\ \text{acid.}}}$$

We have endeavoured to decide this question by experiment; but on account of the greater stability of the benzoic molecule, we have preferred to trace the intermediate acid in the benzoyl-series.

Sulphobenzoic acid, obtained from the acid barium-salt, was evaporated to dryness and heated until it attained the point of quiet fusion. When cold, the acid was coarsely powdered, and mixed with rather more than its own bulk of crystallized sulphuric acid.

It was then heated in a water-bath to a temperature below that at which gases are disengaged. This appeared to be just below 85° C. The substances were kept in contact at this temperature for eight hours. Finally, the mixture was subjected to the heat of boiling water for two hours longer; after which it was treated in the usual way for obtaining the soluble barium-salt.

The salt thus obtained in no manner differed, either in appearance, reaction, or composition, from sulphobenzoate of barium.

Though the above experiments have failed to realize our hopes of producing disulphobenzoic acid, they by no means disprove the existence of this body, and the possibility of producing it under more favourable circumstances. We insist upon this point, on account of the success which has attended our endeavours to trace the existence of disulpho-acids in a perfectly different group of bodies.

We are indebted to M. Gerhardt for the knowledge of a conjugated sulpho-acid, containing an organic base in the place of hydrocarbons, alcohols, acids, &c., which are present in the usual sulpho-acids. Sulphanilic acid, $C_{12}H_7NS_2O_6$, may be viewed as formed by the association of one equivalent of aniline and two equivalents of anhydrous sulphuric acid.

We were curious to ascertain whether this acid, by assimilating once more the elements of anhydrous sulphuric acid, was capable of becoming disulphanilic acid, $C_{12}H_7NS_4O_{12}$.

The existence of disulphobenzolic acid, $C_{12}H_6S_4O_{12}$, the barium-salt of which we have described in the preceding pages, together with the formation of an interesting acid lately obtained by M. Hilkenkamp* in the reaction of sulphite of ammonium on dinitrobenzol, appeared to leave no doubt regarding the existence of a disulphanilic acid. In fact, M. Hilkenkamp's dithiobenzolic acid, $C_{12}H_8N_2S_4O_{12}$, is most intimately connected with the acid we were in search of, as is obvious by a glance at the following Table, in which we have placed a number of known substances in juxta-position with bodies, ideal at present, but the existence of which can no longer be doubted.

Hydrocarbons and substitutes.	Sulpho-acids and substitutes.	Disulpho-acids and substitutes.
$C_{12}H_6$ Benzol.	$C_{12}H_6S_2O_6$ Sulphobenzolic acid.	$C_{12}H_6S_4O_{12}$ Disulphobenzolic acid.
$C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$ Nitrobenzol.	$C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}S_2O_6$ Nitrosulphobenzolic acid.	$C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}S_4O_{12}$
$C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right\}$ Phenylamine. Aniline.	$C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right\}S_2O_6$ Phenylsulphamic acid. Sulphanilic acid.	$C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right\}S_4O_{12}$ Phenyldisulphamic acid. Disulphanilic acid.
$C_{12}\left\{\begin{matrix}H_4\\NO_4\\NO_4\end{matrix}\right\}$ Dinitrobenzol.	$C_{12}\left\{\begin{matrix}H_4\\NO_4\\NO_4\end{matrix}\right\}S_2O_6$	$C_{12}\left\{\begin{matrix}H_4\\NO_4\\NO_4\end{matrix}\right\}S_4O_{12}$
$C_{12}\left\{\begin{matrix}H_4\\NH_2\\NH_2\end{matrix}\right\}$ Phenyldiamine. (Semaniline?)	$C_{12}\left\{\begin{matrix}H_4\\NH_2\\NH_2\end{matrix}\right\}S_2O_6$	$C_{12}\left\{\begin{matrix}H_4\\NH_2\\NH_2\end{matrix}\right\}S_4O_{12}$ Dithiobenzolic acid. Phenyldisulpho-diamic acid.

The preceding synopsis, whilst it fixes, we believe, the correct position of dithiobenzolic acid in the benzol-series, exhibits at the same time its close relation to the disulphanilic acid, which we endeavoured to produce, and the formation of which it may at once be stated succeeded without much difficulty.

Action of Sulphuric Acid upon Aniline.

In order to prepare disulphanilic acid, two parts of strong sulphuric acid were mixed with one part of aniline, when heat was freely evolved, sulphate of aniline being thrown down at the same

* Ann. Ch. Pharm. Neue Reihe, B. xix, S. 86.

time. On further application of heat the salt redissolved, and as the liquid reached the boiling-point it became very dark in colour, sulphurous acid being freely evolved.

In our first experiment the mixture was kept in full ebullition for ten minutes, and then poured into water after it had partially cooled. A confusedly crystalline mass was produced which was well washed with cold water (in which it is not very soluble), and afterwards recrystallized from hot water.

Sulphanilate of Silver.—A portion of this acid was digested with carbonate of silver. The crystalline silver-salt, obtained by evaporating the solution at a low temperature, was dried at 120° and ignited. The silver-percentage led to the formula of sulphanilate of silver,

$$C_{12}(H_6Ag)NS_2O_6.$$

Sulphanilate of Barium.—A barium-salt, prepared in the usual way and submitted to analysis by precipitation by sulphuric acid, gave perfectly analogous results, corresponding to the formula

$$C_{12}(H_6Ba)NS_2O_6.$$

These experiments proved that the acid produced was nothing but M. Gerhardt's well-known sulphanilic acid, the reaction not having gone far enough for the production of the second acid. The treatment with sulphuric acid was therefore resumed. Finely powdered and dry sulphanilic acid, mixed with strong fuming acid to the consistency of a thin paste, was heated in an air-bath to a temperature just approaching that at which sulphurous acid is generated, to 160° and 170° C. This digestion was continued until a portion taken on a glass rod did not solidify on cooling, or give any solid matter when dissolved in a small quantity of water, which happened after the lapse of seven hours, when the mass had the consistency of treacle. It was dissolved in cold water, and separated from a black, almost insoluble matter, which appeared to be somewhat crystalline.

Disulphanilate of Barium.—After saturating with carbonate of barium, the liquid was evaporated to dryness, by which treatment a further separation of the black substance was effected, and the barium-salt was much improved in colour.

If the barium-salt be redissolved and the solution evaporated on the water-bath, a horny substance is formed, which on cooling splits by cracks in all directions; but if the evaporation be completed under the receiver of an air-pump, a mass of microscopic crystals appear, insoluble in alcohol and in ether.

In preparing the new barium-salt, we have found it convenient to precipitate a small portion of the whole liquid by alcohol, and to reject, as retaining generally traces of sulphanilate, the precipitate first formed. Under all circumstances it is very difficult entirely to remove all colouring matter from the solutions of this

salt, which is usually of a pale rose colour. The numbers obtained in the analysis of this salt agree well with the formula of disulphanilate of barium,

$$C_{12}(H_5Ba_2)NS_4O_{12}$$

Disulphanilate of barium blackens without inflaming when heated on foil, in which respect it differs from the sulphanilate, which burns with a bright but smoky flame. Heated in close vessels it furnishes a vapour, which sublimes in beautiful crystals, probably of sulphite of aniline, obtained under similar circumstances from sulphanilic acid.

Disulphanilate of barium is attacked by concentrated nitric acid and gives a yellow liquid, which furnishes on evaporation crystals of a very bitter taste; sulphate of barium is formed at the same time.

Disulphanilic Acid is easily produced from a lead-salt. This substance possesses a very acid and pungent taste; it crystallizes with great difficulty, but is insoluble in alcohol which precipitates strong solutions in white grains. This precipitation is assisted by the addition of a little ether. We have not analysed this body, but we have examined in addition,

Disulphanilate of Silver.—The liquid formed by neutralizing a concentrated solution of the acid with carbonate of silver is precipitated cold by the addition of a mixture of equal volumes of alcohol and ether. The salt subsides in colourless crystalline grains; the deposition is much facilitated by rapidly stirring the contents of the beaker with a glass rod. Disulphanilate of silver crystallizes by spontaneous evaporation of the aqueous solution in small laminæ which blacken and deposit a black powder when boiled with water.

The formula of disulphanilate of silver is—

$$C_{12}\,(H_5Ag_2)\,N\,S_4\,O_{12}.$$

The researches detailed in the preceding paragraphs may serve to characterize more fully a class of compounds of which only a few terms, isolated and scattered in widely differnt groups, had been previously observed. The only disulpho-acids hitherto known, were Berzelius and Laurent's disulphonaphtholic acid and Magnus's ethionic (disulphethylic) acid, and lastly, dithiobenzolic (phenyl-disulphodiamic) acid, recently discovered by M. Hilkenkamp. To these this memoir adds five new acids belonging to several of the most important series of compounds.

Disulphometholic acid . .	$C_2\,H_4\quad S_4\,O_{12}.$
Disulphetholic acid . . .	$C_4\,H_6\quad S_4\,O_{12}.$
Disulphopropiolic acid . .	$C_6\,H_8\quad S_4\,O_{12}.$
Disulphobenzolic acid . .	$C_{12}\,H_6\quad S_4\,O_{12}.$
Disulphanilic acid . . .	$C_{12}\,H_7\,N\,S_4\,O_{12}.$

Our experiments point out, moreover, the universal occurrence and the general mode of formation of these substances. All organic molecules, particularly in the nascent state, appear to be capable of assimilating the elements of either one or two equivalents of anhydrous acid. The formation of the two groups of acids which are thus produced, presents a great analogy with the production of the nitro-substitutes generated under the influence of nitric acid. All these compounds are generated with elimination of water. In the action of nitric acid and sulphuric acid upon benzol, for instance we have

$$\underbrace{C_{12}H_6}_{\text{Benzol.}} + HNO_6 = \underbrace{C_{12}H_5NO_4}_{\text{Nitrobenzol.}} + 2HO.$$

$$\underbrace{C_{12}H_6}_{\text{Benzol.}} + 2HNO_6 = \underbrace{C_{12}H_4N_2O_8}_{\text{Dinitrobenzol.}} + 4HO.$$

$$\underbrace{C_{12}H_6}_{\text{Benzol.}} + H_2S_2O_8 = \underbrace{C_{12}H_6S_2O_6}_{\text{Sulphobenzolic acid.}} + 2HO.$$

$$\underbrace{C_{12}H_6}_{\text{Benzol.}} + 2H_2S_2O_8 = \underbrace{C_{12}H_6S_4O_{12}}_{\text{Disulphobenzolic acid.}} + 4HO.$$

The analogy of these reactions is obvious.

The action of nitric acid upon organic bodies is by no means limited to the production of nitro-compounds, corresponding to nitrobenzol and dinitrobenzol; frequently additional bodies are formed with elimination of 6, 8, and in a few isolated cases, even of 10 equivalents of water. It is possible that analogous sulpho-compounds may exist; hitherto, however, no substances have been observed in which the assimilation of sulphuric acid has gone further than in the disulpho-acids.

Appendix.

During the prosecution of the researches detailed in the preceding paper, our attention was repeatedly called to the substance which M. Liebig has described under the name of *methionic acid*, and which he obtained in the reaction of anhydrous sulphuric acid upon dry ether at low temperatures.* The properties of the barium-salt of this most remarkable acid very closely agree with

* Liebig, Ann. Ch. Pharm. xiii, 32; xxv, 39. Ann. Ch. Phys. i, 59, 189. Wetherill, Ann. Ch. Pharm. lxvi, 122.

those which we observed in studying disulphometholate of barium, although both appeared different in composition. We were repeatedly inclined to admit and to doubt the identity of the two substances. We have now arrived at the conclusion, that methionic and disulphometholic acid are actually *identical*.

The formula adopted by M. Liebig for the barium-salt is

$$CH_3BaS_2O_9.$$

If we double this formula we arrive at the expression

$$C_2H_6BaS_4O_{16}=C_2(H_2Ba_2)S_4O_{12}+4aq,$$

which represents disulphometholate of barium with 4 equivalents of water of crystallization. Our experiments have actually proved that this salt contains indeed 4 equivalents of water, and that this water is retained at 100° C., the temperature at which M. Liebig dried his salt before submitting it to analysis.

More recently M. Redtenbacher and M. Wetherill have investigated the same barium-salt, but neither of them appears to have remarked the fact, that this salt loses water between 100° and 200°. M. Redtenbacher analysed a salt which M. Liebig had prepared himself. M. Wetherill examined a salt which he obtained as a secondary product in his researches on sulphate of ethyl.

Although we had no longer any doubt regarding the identity of methionic acid and disulphometholic acid, we considered it desirable to offer a direct experimental proof of our opinion by a comparison of the barium-salt obtained either by M. Liebig's or by M. Wetherill's process with our new barium-compound. We have, therefore, repeatedly prepared methionate of barium both by M. Liebig's and by M. Wetherill's method. By following exactly the plan described by these chemists, we have actually succeeded in obtaining a salt possessing all the characters of disulphometholate of barium. We did not succeed, however, in obtaining by either of these processes a great quantity of this barium-salt. In both processes, the salt is obviously the product of a secondary reaction.

May 9th, 1856.

Chemical Notices.*

By H. Limpricht.

(Continued from page 189.)

4. *On Sulphocyanide of Benzoyl.*

When chloride of benzoyl and sulphocyanide of potassium are mixed in equal numbers of atoms, great heat is evolved, and the odour of sulphuretted hydrogen becomes perceptible; and on distilling the mixture, a slightly coloured liquid passes over, which becomes colourless after a few rectifications, boils at 191°, and possesses all the properties of benzonitrile; its analysis also gives results agreeing with the composition of that body:

Benzonitrile.		Calc.	Found.
14 C . . .	84	81·6	81·0
5 H . . .	5	4·8	5·1
N . . .	14	13·6	13·4
C_4H_5N . . .	103	100·0	99·5

In all probability, sulphocyanide of benzoyl is first formed, and is afterwards decomposed in the manner shown by the following equation:

$$2(C_{14}H_5O_2,C_2NS_2)=2C_{14}H_5N+2CO_2+2CS_2.$$

5. *Ethylonaphthylamine,* $C_{20}H_8(C_4H_5)N$.

When bromide of ethyl is heated for some hours with naphthylamine in an apparatus which allows the condensed bromine-vapours to flow back again,—or when the two bodies are simply placed in contact for some days at ordinary temperatures, reddish, nodular crystals are formed, consisting of hydrobromate of ethylonaphthylamine, which may be obtained colourless by a few recrystallizations. The colourless crystals, after drying over sulphuric acid, yielded in two experiments 31·5 and 31·7 p.c. bromine, the formula $C_{10}H_8(C_4H_5)N,HBr$ requires 31·7.

Potash added to the solution of this salt separates, not ethylonaphthylamine, but naphthylamine:

$$C_{20}H_8(C_4H_5)N,HBr+KHO_2=\underbrace{C_{20}H_9N}_{\text{Naphthylamine.}}+C_4H_6O_2+KBr.$$

6. *Preparation of Benzamic Acid.*

The action of ferrous acetate on nitro-compounds appears to be always analogous to that of sulphide of ammonium; and accord-

* Ann. Ch. Pharm. xcviii, 117.

ingly, nitrobenzoate of ethyl heated with metallic iron and acetic acid is converted into benzamate of ethyl. The acid separated from the latter by alcoholic potash was converted into a barium-salt, and gave 37·3 p.c. barium, the formula of benzamate of barium requiring 37·4 p.c.

7. *A compound produced from Aldehyde-Ammonia and Chloride of Benzoyl.*

With the view of obtaining compounds analogous to the so-called alcohol-radicals by double decomposition between the aldehyde-ammonias and the chlorides of the acid radicals, ordinary aldehyde-ammonia was brought in contact with chloride of benzoyl; but, instead of the expected compound $\left.\begin{matrix}C_4\ H_3O_2\\C_{14}H_5O_2\end{matrix}\right\}$, which might be formed in the manner represented by the equation

$$\left.\begin{matrix}C_4H_3O_2\\NH_4\end{matrix}\right\} + \left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\} = \left.\begin{matrix}C_4\ H_3O_2\\C_{14}H_5O_2\end{matrix}\right\} + NH_4Cl,$$

a body was formed having the composition, $C_{32}H_{16}N_2O_4$; its mode of formation, however, is not at present intelligible.

For the preparation of this substance, finely pulverized aldehyde-ammonia must be added to chloride of benzoyl by very small portions, so as to avoid heating. and the consequent formation of brown resinous products, t[illegible]dditions being continued till the mass has become solid; the mixture must then be left to stand for some hours, washed with water to remove sal-ammoniac, and with carbonate of soda to remove benzoic acid. The residue is dissolved in hot alcohol, and the solution on cooling deposits long delicate needles united in concentric groups; the mother-liquor yields the same crystals to the last drop.

The compound is insoluble in water, dissolves sparingly in alcohol and ether in the cold, but freely with the aid of heat; melts when heated, and sublimes at a higher temperature, partly without decomposition.

Heated with potash-ley, it is decomposed very slowly, giving off ammonia, and depositing a brown resin, like resin of aldehyde; and the potash-solution contains benzoic acid.

It is not altered by heating with peroxide of lead and water; but if a little sulphuric acid is added, aldehyde is evolved, and the liquid filtered while hot deposits crystals of benzamide.

When the compound is stirred up with water through which nitrous acid is passed, aldehyde is also formed together with benzamide.

Strong sulphuric acid heated with the compound dissolves it, forming a brown solution; on addition of water, a brown resin,

separates out, and the liquid filtered while hot yields crystals of benzoic acid.

When it is boiled, in alcoholic solution or suspended in water, with carbonate of silver or mercuric oxide, neither of these compounds is either dissolved or reduced. The alcoholic solution is not precipitated by nitrate of silver, even with addition of ammonia.

The rational formula of the substance cannot at present be determined. It may be observed, however, that the empirical formula above given contains the elements of benzamide and cinnamide:

$$\underbrace{C_{18}H_9NO_2}_{\text{Cinnamide.}} + \underbrace{C_{14}H_7NO_2}_{\text{Benzamide.}} = C_{32}H_{16}N_2O_4;$$

and that the numbers found by Schwartz for hipparaffin, viz., 71·4 C, 6·1 H, and 10·5 N agree nearly with the composition of the new compound, which gives, as a mean, 71·7 C, 6·3 H, and 10·4 N.

On a New Mode of Formation of Hydride of Benzoyl.*

By H. Kolbe.

Chemists are now pretty generally agreed that benzoic acid, chloride of benzoyl, cyanide of benzoyl, &c., should be regarded as compounds of the oxygenated radical, $C_{14}H_5O_2$ or $(C_{12}H_5)C_2O_2$. Respecting the constitution of bitter-almond oil, however, there is still some doubt; some being inclined to regard that body as $C_{14}H_5O_2,H$, others as $C_{14}H_5O,HO$. If the former view be correct, it is to be expected that this body will be formed by the action of nascent hydrogen on the chloride or cyanide of benzoyl. Experiments in this direction have indeed been already made by Chiozza,† who finds that when chloride of benzoyl is poured upon hydride of copper (Cu_2H), subchloride of copper is formed, and the liquid, after the excess of chloride of benzoyl has been removed by water, exhibits a distinct odour of bitter-almond oil. The quantity obtained, however, was not sufficient for complete identification.

The action of hydrochloric acid and zinc on the chloride of benzoyl is not adapted for the production of the hydride, because the chloride is too quickly resolved into benzoic and hydrochloric acids, to allow the nascent hydrogen to act upon it; but the cyanide,

* Ann. Ch. Pharm. xcviii. 345. † Ann. Ch. Pharm. lxxxv. 232.

which is much less rapidly decomposed by water than the chloride, gives better results.

When pure crystallised cyanide of benzoyl is mixed in a tubulated retort, with hydrochloric acid, and heated till it melts, and pieces of granulated zinc are introduced from time to time, a rapid evolution of gas takes place at first; but this soon ceases, especially if the liquid be shaken, so as to bring the cyanide of benzoyl, which floats on the surface, in contact with the metal. If the addition of zinc be continued, the colourless cyanide of benzoyl begins, after a while, to assume a yellow tint where it adheres to the metal. At the same time a strong odour of hydrocyanic acid is evolved, and, as the decomposition of the cyanide of benzoyl proceeds, the odour of bitter-almond oil likewise becomes distinctly perceptible. To effect the complete resolution of the cyanide of benzoyl into hydrocyanic acid and hydride of benzoyl, a considerable quantity of zinc is required. Towards the end of the operation, the zinc becomes covered with a dirty yellow, greasy mass, which ultimately, when all the oil-drops have disappeared from the surface of the chloride of zinc solution, completely envelops the metal.

When this greasy substance is separated from the supernatant acid saline solution, which contains but a small quantity of benzoic acid, and then heated with excess of ordinary potash-ley, it is decomposed, and converted into yellowish-red oily drops, which diffuse the pure odour of bitter-almond oil, the pieces of zinc, at the same time, appearing with a bright metallic surface. On distilling this alkaline mass, pure hydride of benzoyl first passes over into the receiver in considerable quantity, in the form of an oily body, together with the water; at a later stage of the process, the milky distillate contains benzoin, the greater part of which, however, is contained in the alkaline residue. The oily distillate, after being separated from the water by a pipette, further dehydrated by chloride of calcium, and distilled in a bulb-apparatus like that used by Bunsen for the preparation and purification of cacodyl, was perfectly transparent and colourless; exhibited the composition and properties of bitter-almond oil; and solidified to a crystalline mass with bisulphite of soda.

The turbid alkaline liquid remaining in the retort and containing benzoin, was poured, when cold, from the metallic zinc and filtered. The filtrate yielded, on addition of hydrochloric acid, a somewhat copious precipitate of benzoic acid, and, at the same time, hydrocyanic acid was set free. The dirty grey substance remaining on the filter, when likewise treated with hydrochloric acid, left impure benzoin, which, after recrystallisation from boiling alcohol, exhibited the composition and properties of the pure substance.

To prevent the transformation of the hydride of benzoyl into benzoin, and to determine how much hydride of benzoyl can be

obtained, under the most favourable circumstances, from a given quantity of the cyanide, another portion (obtained from 30 grms. of cyanide of benzoyl) of the yellow, greasy mass surrounding the pieces of zinc, was distilled with excess of milk of lime, after addition of protosulphate of iron; but not a trace of hydride of benzoyl was obtained. It seems probable, therefore, that the yellow mass does not contain the hydride of benzoyl in the form of a mere mixture; but that it is a chemical compound, perhaps the oily compound of hydride of benzoyl and hydrocyanic acid described by Völckel*, made thicker in the present instance by admixture of benzoic acid. This compound, which is decomposed by potash, appears to resist the action of hydrate of lime.

The conversion of cyanide of benzoyl into hydrocyanic acid and hydride of benzoyl likewise takes place, though much more slowly, by continued gentle heating with metallic mercury and hydrochloric acid (better and more quickly, perhaps, in a sealed tube).

On some Compounds of Benzoyl.†

By Carl Voit.

The compounds of benzamic acid with bases have not hitherto been much studied, only the silver-salt having been analysed by Chancel, and a few compounds of benzamic acid with other acids, in which it appears to play the part of a base, having been studied by Gerland. The behaviour of binitrobenzoic acid with sulphuretted hydrogen was likewise unknown, and it could not be determined beforehand, whether both equivalents of hyponitric acid, or only one, would be replaced by amidogen. The following experiments were undertaken to supply these deficiencies.

Nitrobenzoic acid was prepared by adding fused benzoic acid, in small portions, to a mixture of 2 pts. concentrated sulphuric acid, 1 pt. nitric acid (sp. gr. 1·5), and heating the mixture gently for about half an hour; no binitrobenzoic acid is thereby produced, that acid being, in fact, much less easy to obtain than is commonly supposed; but on adding water to the mixture, nitrobenzoic acid is precipitated in white flakes.

When chloride of benzoyl is dropped into the mixture of sulphuric and nitric acid, the liquid becomes heated, and gives off chlorine, together with another gas which attacks the eyes powerfully; water then throws down white flakes, which were found, by analysis, to be pure nitrobenzoic acid.

* Pogg. Ann. lxii. 444.
† Ann. Ch. Pharm. xcviii. 100.

The nitrobenzoic acid was transformed by the usual method of boiling with sulphide of ammonium, into *amidobenzoic* or benzamic acid;* and, on adding strong hydrochloric acid to the liquid, after it had been decanted from the precipitated sulphur and evaporated, hydrochlorate of amidobenzoic acid was precipitated in needles united in nodular groups; this compound served for the preparation of the following salts:—

Amidobenzoate of Soda, $C_{14}H_4Na(NH_2)O_4$ (at 100°).—From the hot concentrated solution of the baryta-salt, the baryta was precipitated by an equivalent quantity of sulphate of soda, and the filtrate evaporated to dryness. This soda-salt is so very soluble in water, that it is difficult to get it well crystallised. The concentrated solution was therefore mixed with absolute alcohol, and the resulting white crystalline magma pressed between paper, and dried at 100°. Under the microscope it appeared to consist of needle-shaped crystals.

	Calculated.	Found.
Soda . . .	19·50	19·13

Amidobenzoate of Baryta, $C_{14}H_4Ba(NH_2)O_4$ (at 100°).—The aqueous solution of hydrochlorate of amidobenzoic acid was neutralised with carbonate of baryta, and the hot filtrate evaporated over the water-bath; at a certain degree of concentration, it deposits large pale reddish prisms, which cannot be completely decolorised, even by repeated crystallisation, with addition of animal charcoal, but yield a pure white powder.

		Calc.	Found.
14 C	84·0	41·07	41·12
6 H	6·0	2·93	3·51
Ba	68·5	33·50	33·20
N	14·0	6·84	
4 O	32·0	15·66	
$C_{14}H_4Ba(NH_2)O_4$ . .	204·5	100·00	

Amidobenzoate of Strontia, $C_{14}H_4S_2(NH_2)O_4+2aq.$ — The aqueous solution of the baryta-salt was precipitated with sulphuric acid; and the filtrate mixed with hydrate of strontia, till a slight alkaline reaction was produced, and evaporated. It then deposited prisms having a faint reddish colour, but becoming white by recrystallisation. They dissolve very readily in water, slowly in alcohol, and give off their water of crystallisation at 100°.

	Calc.	Found.
Water . .	9·10	8·78
Strontia . .	28·81	28·58

* The author objects to the ordinary name benzamic acid, because it is only the radicals of bibasic acids which can form acids to which the termination *amic* can be properly applied.

Amidobenzoate of Lime, $C_{14}H_4Ca(NH_2)O_4$.—Hydrochlorate of benzoic acid was boiled with milk of lime, and the filtrate evaporated. The concentrated liquid soon deposited delicate white needles, which turned red on exposure to the air; they were once recrystallised from hot alcohol, then quickly pressed and dried at 100°.

	Calc.	Found.
Lime . . .	17·95	17·61

Amidobenzoate of Magnesia, $C_{14}H_4Mg(NH_2)O_4 + 7aq.$ — By double decomposition between the baryta-salt and sulphate of magnesia, this salt is obtained in large, transparent, six-sided prisms, with oblique truncation-face; it decomposes quickly on exposure to the air.

	Calc.	Found.	
Water . . .	29·86	29·36	
Magnesia . . .	13·51	13·65	13·07

Binitrobenzoic acid was obtained by Cahours, by gently heating benzoic acid for an hour, with a mixture of sulphuric and nitric acid. Voit obtained, by this process, only nitrobenzoic acid, or a mixture of that acid with binitrobenzoic, and found it necessary to boil for six hours longer, with sulphuric and nitric acid, in order to convert the nitrobenzoic into binitrobenzoic acid. At the beginning of the operation, the evolution of nitrous acid is so violent that, unless the heat is well regulated, the mixture is very apt to froth over; but at length a point is attained, when red fumes are no longer evolved. If the liquid be then left to cool, the binitrobenzoic acid separates almost completely in shining crystals; if the heat be longer continued, vapours are evolved which excite coughing; the liquid assumes a darker colour; and the binitrobenzoic acid, which separates on cooling, is likewise coloured. Binitrobenzoic acid is much less soluble in water, either hot or cold, than nitrobenzoic acid: carbonate of soda dissolves it, forming a red solution. By boiling with water and carbonate of baryta, the baryta-salt was obtained, and settled down from the hot filtrate on cooling in yellowish crystalline nodules. It yielded by analysis, 27·35 and 27·17 p.c. baryta, agreeing with the formula $C_{14}H_3Ba(NO_4)_2O_4$, which requires 27·37.

Binitrobenzoate of ethyl is easily produced, by heating binitrobenzoic acid with alcohol and sulphuric acid, and forms oily drops, which solidify on cooling. It dissolves readily in hot, very sparingly in cold alcohol, so that the alcoholic solution, when filtered hot, solidifies to a magma consisting of silky needles. On attempting to prepare biamidobenzamide, by digesting this ether with sulphide of ammonium, sulphur was deposited in considerable quantity, and the filtrate, when evaporated, yielded a crystalline

mass, which, however, could not be obtained sufficiently pure for analysis.

On the other hand, binitrobenzoate of ethyl is readily converted into *binitrobenzamide* by digesting it for several days with alcoholic ammonia, which dissolves it with blood-red colour, and after concentration deposits the amide in prisms and laminæ having a faint yellowish colour and fatty lustre. Binitrobenzamide dissolves sparingly in cold, somewhat more readily in hot water, forming a solution which has a bitter taste and neutral reaction. It melts at 183°, and decomposes at a higher temperature without subliming. The ammoniacal solution forms no precipitate with nitrate of silver.

Binitrobenzamide.		Calc.	Found.
14 C	84	39·81	40·87
5 H	5	2·37	2·88
2 NO_4	92	43·60	
N	14	6·63	6·90
2 O	16	7·59	
N $\left\{ \begin{matrix} C_{14}H_3(NO_4)_2O_2 \\ H \\ H \end{matrix} \right.$	211	100·00	

To convert the binitrobenzoic acid into *Biamidobenzoic* acid, sulphuretted hydrogen was passed continuously through the hot ammoniacal solution; the solution filtered from sulphur, evaporated over the water-bath, supersaturated with hydrochloric acid, and again filtered hot: the filtrate after a while deposited green crystals of hydrochlorate of biamidobenzoic acid.

Biamidobenzoic acid, obtained by digesting the aqueous solution of the sulphate with carbonate of baryta, and evaporating the filtrate, first over the water-bath, and afterwards over sulphuric acid, forms small, greenish, acuminated crystals, which dissolve readily in water, alcohol, and ether; have no taste and no reaction upon vegetable colours; melt and blacken at about 195°; and cannot be sublimed.

It is remarkable that biamidobenzoic acid does not combine with bases, but forms well crystallized compounds with acids, whence the name of acid is not very appropriate for it. In this respect, it exhibits the behaviour which is seen so remarkably in aniline, viz., that the substitution-products retain in general the character of the compound from which they are derived; but, nevertheless, the substance which enters does not completely lose its chemical character, but impresses that character on the substitution-product, the more strongly as the number of hydrogen-atoms replaced by it is greater. Benzoic acid is a strong acid; the introduction even of one atom of the basic substance, amidogen, causes it already to exhibit basic properties, for amidobenzoic acid

unites with acids as well as with bases; while with the second atom of amidogen, the acid qualities completely disappear, the product biamidobenzoic acid forming salts only with acids.

Hydrochlorate of Biamidobenzoic Acid, $C_{14}H_4(NH_2)_2O_4,2HCl$.—The impure compound obtained in the preparation of biamidobenzoic acid, is not easily purified by recrystallization; a pure salt is more easily prepared by mixing the solution in a small quantity of water with strong hydrochloric acid; in that case, either white needles are immediately deposited, or a flocculent precipitate is first produced which afterwards changes to the same needles. Should the salt be not yet perfectly pure, the operation must be repeated. Hydrochlorate of biamidobenzoic acid is very soluble in water, alcohol, and ether; the aqueous solution decomposes on exposure to the air, depositing black flocks. The dry compound melts when heated, then decomposes, and yields a sublimate of sal-ammoniac. For analysis, the salt, after being pressed between paper, was dried, first over sulphuric acid, then at 60°.

	Calc.	Found.	
Chlorine	31·55	31·02	31·10

Bichloride of platinum does not form any precipitate in the aqueous solution, even on addition of alcohol and ether; but when the mixture is left to evaporate over sulphuric acid, it deposits brown crusts, which after drying yield a greyish-white powder. Its composition appears to be $C_{14}H_4(NH_2)_2O_4,2HCl,PtCl_2$; for it yielded 24·83 p.c. platinum, and the formula requires 25·01 p.c. If it were analogous to the platinum-salts of other bases which saturate 2 equivalents of acid (*e.g.*, quinine, cinchonine), it would contain 2 eq. $PtCl_2$.

Sulphate of Biamidobenzoic acid, $C_{14}H_4(NH_2)_2O_4,S_2H_2O_8$.—The hydrochlorate was dissolved in dilute sulphuric acid and the solution concentrated; the still brownish tables and laminæ which separated, were obtained nearly colourless by recrystallization from alcohol. They dissolve readily in water, somewhat less in alcohol; the solutions decompose very readily, and appear brownish-yellow by transmitted, grass-green by reflected, light.

Crystals dried over Sulphuric acid.			Found	
14 C	84	33·60	34·33	33·55
10 H	10	4·00	4·65	4·93
2 N	28	11·20	11·29	10·94
6 O	48	19·20		
2 SO_3.	80	32·00	32·25	32·68
$C_{14}H_4(NH_2)_2O_4,S_2H_2O_8$.	250	100·00		

Nitrate of Biamidobenzoic acid. — Obtained by decomposing

the sulphate with nitrate of baryta; separates in dark-coloured crystals.

Acetate of Biamidobenzoic acid, was prepared by precipitating the sulphate with acetate of baryta. The solution became decomposed during evaporation, and deposited a brown powder; but by further evaporation of the filtered liquid, brownish prisms were obtained.

Oxalate of Biamidobenzoic acid forms brown needles, which are obtained by evaporating the hydrochlorate with oxalic acid.

Biamidobenzoic acid was heated to 100° in a sealed tube with iodide of ethyl, with the view of obtaining biamidobenzoate of ethyl; the mass became solid; but on addition of hydrochloric acid to the aqueous solution, white needles were obtained, which proved to be nothing but hydrochlorate of biamidobenzoic acid.

By decomposing biamidobenzoic acid in hot aqueous solution with nitrous acid, which, according to Gerland, converts amidobenzoic into oxybenzoic acid, only a red, resinous, uncrystallizable mass was obtained, although the passage of the gas was continued for several days.

On some Constituents of Opium*.

By T. Anderson.

The following experiments, which are a continuation of Dr. Anderson's researches upon opium already reported in this Journal (v, 257; viii, 283), relate chiefly to meconine, its identity with opianyl, and various substitution-products of that substance.

Meconine.—The mother-liquor from which narceine (v. 258) had crystallized out, yielded after being concentrated and left at rest, nothing but granular crystals of sal-ammoniac. To obtain meconine from this liquid, it was mixed in large bottles, with $\frac{1}{5}$ of its bulk of ether; the bottles tightly corked, left to stand in a warm place at about 26° C., and frequently shaken; the ethereal layer then separated; and this treatment several times repeated with fresh ether. The extracts obtained with the first portions of ether, left, after the ether had been distilled off, a brown syrupy residue which yielded no crystals, even after standing for several days; the extracts with the latter portions of ether often left residues in which crystals formed after standing. On adding water to these residues, a viscid substance of the consistence of turpentine separated out; and this substance when treated with hydrochloric acid partly dissolved, while the undissolved portion was converted into a dark grey crystalline powder. The latter was impure meconine;

* Ed. Phil. Trans. xxi, [1], 204. Ann. Ch. Pharm. xcviii, 44.

the hydrochloric acid solution contained papaverine. The meconine was separated, by solution in boiling water, from an indifferent resinous body; and the solution on cooling deposited the meconine in yellowish needle-shaped crystals, which were further purified by recrystallization with addition of animal charcoal.

Pure meconine crystallizes from its aqueous solution in white shining needles. It dissolves in 22 times its weight of boiling water, and in 700 times its weight of water at 15·5 C. (60° F.). It is likewise soluble in alcohol and ether. Has a bitter taste. Melts at 110° C. in the dry state; at 77° under water; when carefully raised to a higher temperature, it volatilizes without residue, and sublimes in beautiful crystals. It does not appear to dissolve in alkaline liquids more readily than in water. Does not combine with metallic oxides; is not precipitated by subacetate of lead. Anderson's analyses of meconine agree nearly with those of Couerbe* and Regnault†, when the latter are calculated according to the atomic weights now adopted, and lead to the formula $C_{10}H_5O_4$ or $C_{20}H_{10}O_8$, which latter Anderson also found for opianyl‡, the substance obtained by the action of nitric acid upon narcotine.

Meconine.		Calc.	Found.	
20 C . . .	120	61·85	61·40	61·50
10 H . . .	10	5·15	5·12	5·13
8 O . . .	64	33·00	33·48	33·37
$C_{25}H_{10}O_8$.	194	100·00	100·00	100·00

Meconine and opianyl are likewise identical in properties. Sulphuric acid produces with the former, even in the cold, a colourless solution which assumes a deep purple colour when heated; water added to this solution turns it brown, and separates a dark brown precipitate, which dissolves with red colour in alcohol. Of the two names given to this substance, Anderson gives the preference to *Opianyl.*

Action of Nitric acid upon Opianyl.—Opianyl dissolves abundantly in cold concentrated nitric acid; on heating the liquid, red vapours are evolved in small quantity. The solution diluted with water deposits bulky crystals, which may be purified by washing and recrystallization from boiling alcohol. *Nitropianyl* thus prepared forms white needles and prisms. It dissolves but sparingly in cold, somewhat more freely in boiling water; much more readily in boiling alcohol; dissolves also in ether. All these solutions are colourless and neutral to test-paper. Nitropianyl melts at 160° C., forming a transparent liquid, which solidifies in a crystalline mass on cooling. Heated in small quantities on platinum-foil, it volatilizes without decomposition, leaving only a small carbonaceous

* Ann. Ch. Pharm. xvii, 167. † Ann. Ch. Pharm. xxix, 314.
‡ Ann. Ch. Pharm. lxxxvi, 191.

residue; but when heated in a small glass-tube, it decomposes suddenly, and leaves a bulky, porous, carbonaceous residue. It is not precipitated by metallic salts. It does not dissolve more abundantly in cold solution of potash or ammonia than in pure water; but at the boiling heat, it dissolves in considerable quantity, and with decomposition, forming a yellow liquid which does not deposit anything on cooling, or on addition of hydrochloric acid. It is insoluble in hydrochloric acid; dissolves in cold strong nitric acid; and separates out in crystalline flakes when the solution is diluted. The crystals of nitropianyl immediately assume a yellow colour when acted upon by strong sulphuric acid, and dissolve to a red liquid when heated. The composition of nitropianyl is $C_{20}H_9(NO_4)O_8$; the same formula was assigned by Couerbe to his hyponitromeconic acid, which, however, differs from Anderson's nitropianyl in certain properties, and, according to Anderson, is not obtained by the process given by Couerbe.

	Nitropianyl.	Calc.	Found.
20 C	120	50·20	50·11
9 H	9	3·76	3·92
N	14	5·85	
12 O	96	40·19	
$C_{20}H_9(NO_4)O_8$	239	100·00	

Action of Chlorine upon Opianyl.—When chlorine gas is passed into a cold-saturated aqueous solution of opianyl, crystals of *Chloropianyl* soon separate in considerable quantities; this compound may also be obtained by passing dry chlorine over fused opianyl.—Chloropianyl purified by recrystallization from alcohol, forms colourless needles which are nearly insoluble in cold water; dissolve somewhat more easily in boiling water; abundantly in alcohol and ether. Alkaline liquids do not dissolve more of it than water, and do not extract chlorine from it; nitric acid dissolves it with red colour, and decomposes it when heated; strong sulphuric acid dissolves it in the cold, and the solution when heated assumes a greenish-blue colour, and on subsequent addition of water, deposits brown flakes soluble with a red colour in alkalies. Chloropianyl melts at 175° C., and sublimes without decomposition at a higher temperature. The properties of chloropianyl are the same, whether it is obtained from opianyl which has been prepared from narcotine, or from opianyl obtained directly from opium.

	Opianyl.	Calc.	Found.		
20 C	120·0	52·51	52·40	52·35	52·60
9 H	9·0	3·93	4·32	4·21	4·20
Cl	35·5	15·53	15·17		
8 O	64·0	28·03	28·11		
$C_{20}H_9ClO_8$	228·5	100·00	100·00		

Couerbe describes, as the product of the action of chlorine upon meconine, a resinous substance which Anderson believes to be bichloropianyl.

Action of Bromine on Opianyl.—When bromine-water is gradually added to an aqueous solution of opianyl, crystals gradually separate, consisting of *Bromopianyl*, which may be purified by recrystallization. The compound then forms colourless needles, which dissolve sparingly in water, abundantly in alcohol and ether. Bromopianyl melts at 167° C. In its properties it closely resembles chloropianyl.

Bromopianyl.		Calc.	Found.
20 C	120	43·95	43·81
9 H	9	3·29	3·40
Br	80	29·30	29·21
8 O	64	23·46	23·58
$C_{20}H_9BrO_8$	273	100·00	100·00

Action of Chloride of Iodine upon Opianyl.—Iodine does not act upon opianyl, either in alcoholic solution or in the solid form. An iodated substitution-product is, however, obtained by adding chloride of iodine to an aqueous solution of opianyl, and leaving the liquid in a warm place for some days; long crystals of *Iodopianyl* are then formed, somewhat contaminated by free iodine separated at the same time. Iodopianyl recrystallized from boiling alcohol forms colourless needles, which are scarcely soluble in water, but dissolve more freely in alcohol and in ether. It melts at 112° C., forming a liquid which is colourless at first, but afterwards turns brown; at a higher temperature, it decomposes with volatilization of iodine. Nitric acid likewise decomposes it with separation of iodine. Sulphuric acid dissolves it, and the solution assumes a dark colour when heated.

Iodopianyl.		Calc.	Found.
20 C	120·0	37·48	37·16
9 H	9·0	2·81	2·96
I	127·1	39·70	39·48
8 O	64·0	20·01	20·40
$C_{20}H_9IO_8$	320·1	100·00	100·00

Action of Sulphuric acid and Peroxide of Lead upon Opianyl.—When opianyl is gently heated with peroxide of lead and sulphuric acid, carbonic acid is evolved, and an amorphous substance remains in solution. The reaction was not further investigated, in consequence of deficiency of material; the author expected to find opianic and hemipinic acids among the products of the oxidation.

The identity of meconine, which exists ready formed in opium, with opianyl, an artificial product obtained from narcotine, may furnish a starting point in the examination of the relations which

exist between the several constituents of opium. It has long been observed, that those proximate principles of a plant which occur together frequently exhibit a certain similarity in their composition or origin. Thus quinine and cinchonine, which differ only in the number of oxygen-atoms, may be compared with different oxides of the same metal; and again, of the two bases which occur in the seeds of *Peganum Harmala*, the one may be converted into the other by the action of oxidizing agents. Many cases may also be cited in which the formulæ of two simultaneously occurring bases agree in the amounts of certain of their constituents. Thus morphine and codeine differ only by C_2H_2, like two homologous substances, although they do not exhibit that degree of similarity in their properties which is generally found in homologous compounds. Thebaine, $C_{38}H_{21}NO_6$, and codeine, $C_{36}H_{21}NO_6$, differ by 2C; thebaine, and papaverine, $C_{40}H_{21}NO_8$, by C_2O_2; narceine, $C_{46}H_{29}NO_{10}$, and narcotine, $C_{46}H_{25}NO_{14}$, by 4HO.

Anderson had formerly remarked* that narcotine may be regarded as a compound of cotarnine and a hypothetical *hydruret of opianyl*. He thinks it possible that the opianine examined by Hinterberger† may have a similar constitution, and that Hinterberger's analyses may be made consistent with the formula $C_{66}H_{37}NO_{22}$. In that case, the relations between opianine, narcotine, and narcogenine are as follows:

		Cotarnine.	Hydruret of Opianyl.
Opianine . .	$C_{66}H_{37}NO_{22}$ =	$C_{26}H_{13}NO_6$ +	$2C_{20}H_{12}O_8$
Narcotine . .	$C_{46}H_{25}NO_{14}$ =	$C_{26}H_{13}NO_6$ +	$C_{20}H_{12}O_8$
Narcogenine .	$2(C_{36}H_{19}NO_{10})$ =	$2(C_{26}H_{13}NO_6)$ +	$C_{20}H_{12}O_8$

Anderson likewise draws attention to a remarkable fact which was brought to light in investigating the action of sulphuric acid upon opianic acid. In this reaction, there is produced a true dye-stuff, which yields with alumina and iron mordants all the colours that are obtained by the use of madder. Now as alizarin, $C_{20}H_6O_6$, differs from opianic acid only by 4 Aq., Anderson thinks it not improbable that the new colouring matter may be identical with alizarin.

* Chem. Soc. Qu. J., v, 264.

† Ann. Ch. Pharm. lxxvii, 207; lxxxii, 320. Anderson regards the amount of nitrogen in opianine given in the former of these communications as the more correct.

On the Compounds of Stibethyl. *

By W. Merck.

Löwig and Schweizer, in their investigation of the compounds of stibethyl,† arrived at the conclusion that the radical $(C_4H_5)_3Sb$ combines with 2 At. of an electronegative body; *e. g.*, the oxide $= (C_4H_5)_3Sb,O_2$; the iodide $= (C_4H_5)_3Sb,I_2$, &c. Similar formulæ were subsequently given by Landolt for the compounds of arsentriethyl $(C_4H_5)_3As$, by Cahours and Riche for those of arsentrimethyl, and by Berlé for those of stibtriamyl. On the other hand, it was found that arsenbimethyl (cacodyl) $(C_2H_3)_2As$, and arsenbiethyl $(C_4H_5)_2Sb$, as well as arsenethylium $(C_4H_5)_4As$, and stibethylium $(C_4H_5)_4Sb$, unite with only 1 At. of an electronegative body; and hence arose a doubt as to whether the stibethyl compounds were constituted as above mentioned, or whether they did not rather contain 1 At. hydrogen more, *e. g.*, the iodide $= (C_4H_5)_3Sb,I + HI$ or $(C_4H_5)_3HSb,I_2$. As, however, the percentage composition, according to the more recently proposed formula, differs but little from that deduced from the older one, and therefore the comparative merits of the two cannot be determined by direct analysis, the following experiments on the action of ammonia and of stibethyl on the iodide of stibethyl, were undertaken with the view of deciding the question.

The experiments on the action of ammonia on iodide of stibethyl did not lead to any decisive results. When the solutions of the two bodies in absolute alcohol are mixed, the whole remains clear and colourless; on evaporating the mixture in vacuo over sulphuric acid, the excess of ammonia escapes first, then a salt crystallizes out in regular octohedrons containing 37 per cent. iodine (the iodide of stibtriethyl presently to be noticed), and at last iodide of ammonium.

The action of stibethyl on the iodide was next tried. One-half of an ethereal solution of stibethyl, prepared out of contact of air, was exactly saturated with iodine, the other half then added, and the mixture left to evaporate in an atmosphere of carbonic acid. There were then formed—first, the octohedral crystals of iodide of stibtriethyl $(SbAe_3)I$, but afterwards smaller and more soluble crystals, having a different form; these last are regarded by Merck as $(SbAe_3H)I$. [The radical contained in them, viz., $(C_4H_5)_3HSb$, Löwig denotes by the name *stibtriethylamine.*] The latter crystals yielded from 36·52 to 36·84 per cent. iodine, while the formula $(SbAe_3H)I$, requires 36·92. Now the action of stibethyl on the so-called iodide of stibethyl might be repre-

* J. pr. Chem. lxvi. 56; Ann. Ch. Pharm., xcvii, 329.
† Ann. Ch. Pharm. lxxv, 315. Chem. Soc. Qu. J., v, 69.

sented by one or other of the following equations, according to the formula adopted for the iodide:—

(1). $(SbAe_3)I_2 + SbAe_3 = 2(SbAe_3)I$

(2). $(SbAe_3)I_2 + SbAe_3 = (SbAe_4)I + (SbAe_2)I$

(3). $\left.\begin{matrix}(SbAe_3)I,HI \\ \text{or } (SbAe_3H)I_2\end{matrix}\right\} + SbAe_3 = (SbAe_3H)I + (SbAe_3)I.$

It will easily be seen that the results of the above experiments agree with equation (3), but are inconsistent with (1) and (2). [The formula $(SbAe_2)I$, requires 40·26 per cent. iodine.] Hence the formula of iodide of stibethyl must be either $(SbAe_3),I + HI$, or $(SbAe_3H)I_2$. This is further proved by several reactions, among which may be cited the momentary formation of the so-called iodide of stibethyl on adding hydriodic acid to a solution of the salt $(SbAe_3)I$. Merck does not, however, explain how the compound $(SbAe_3)I + HI$ can be formed by the direct combination of iodine with stibethyl dissolved in alcohol or ether.

Compounds of Stibtriethyl.

Oxide. $SbAe_3O$.—This compound is obtained by decomposing the aqueous solution of the iodide with pure and recently precipitated oxide of silver. The filtrate contains in solution a somewhat considerable quantity of oxide of silver, which can only be partially separated by concentration, and must therefore be removed by careful precipitation with dilute hydriodic acid. Hydrochloric acid cannot be used, because it dissolves the oxide in somewhat considerable quantity. The filtered solution is then evaporated, first over the water-bath, and afterwards in vacuo over oil of vitriol.

Thick, syrupy, transparent, colourless mass, which has a slippery feel between the fingers, like very strong potash-ley. It is inodorous; has an intensely bitter and biting taste, and a strong alkaline reaction. It is somewhat volatile, slight fumes being produced when a rod moistened with hydrochloric acid is held over its aqueous solution: it does not, however, diminish perceptibly in weight when kept even for a long time in vacuo over sulphuric acid.

The oxide dissolves readily in water, the solution being attended with considerable rise of temperature. The solution precipitates manganous, ferrous, ferric, cupric, mercuric and lead salts, without dissolving the precipitates in excess. In alumina and zinc salts, it forms white precipitates, soluble in excess.

Oxide of stibtriethyl is a strong base; its salts all dissolve readily in water, but sparingly in alcohol: they have a bitter taste, but no emetic action.

The oxide dissolves readily in alcohol, but sparingly in ether.

The *Sulphide of stibtriethyl* has not yet been obtained in the

separate state. On saturating an alcoholic solution of the oxide with sulphuretted hydrogen and leaving it to evaporate, fine crystals are obtained, which appear to be identical with the so-called sulphide of stibethyl.

Carbonate of Stibtriethyl. $SbAe_3O,CO_2$.—Obtained by decomposing the iodide with carbonate of silver. On evaporating the filtrate over the water-bath, the salt remains in the form of a syrupy mass, without any trace of crystallization.

Sulphate of Stibtriethyl. $SbAe_3O,SO_3$.—Obtained by decomposing the iodide with sulphate of silver. Does not crystallize; but by evaporation, first in the water-bath and then in vacuo over oil of vitriol, it is obtained in the form of a transparent gummy mass, which may be rubbed to a white powder. Deliquesces readily in the air, and dissolves in all proportions in water.

Iodide of Stibtriethyl. $SbAe_3I$.—Obtained either by exactly saturating the oxide with hydriodic acid, the latter being added in the state of dilute solution, till it produces a permanent cloud, which may then be made to disappear by adding a drop of the oxide; or by the action of ammonia or stibtriethyl on iodide of stibtriethyl and hydrogen, $SbAe_3I,HI$.

Crystallizes very readily. By leaving the ethereal solution to evaporate, large, hard, transparent, colourless, octohedrons or tetrahedrons are obtained, which are inodorous, and have a glassy lustre. They exhibit no trace of decomposition when exposed to the air, even for weeks; they are anhydrous, and suffer no loss of weight in vacuo oil of vitriol. Crystals of the same form are obtained from the aqueous or alcoholic solution.

		Calc.	Found.			
			a.	*b.*	*c.*	*d.*
Sb . . .	129	37·72	37·84			
12 C . . .	72	21·05	20·69	20·65	20·70	
15 H . . .	15	4·39	4·53	4·63	4·52	
I . . .	126	36·84	36·68	37·70	37·10	36·93
$(C_4H_5)_3SbI$.	342	100·00	99·74			

a and *b* were obtained by the action of ammonia; *c* and *d* by that of stibethyl on the compound, $SbAe_3I,HI$.

An aqueous solution of mercuric bromide added to aqueous iodide of stibtriethyl, forms at first a yellow precipitate, which, however, very soon changes to red, the decomposition being then complete. No doubt the yellow modification of mercuric iodide is formed at first, and afterwards passes into the red. This reaction distinguishes iodide of stibtriethyl from iodide of stibethylium. When the bromide of mercury and iodide of stibtriethyl are mixed in exactly equal numbers of atoms and in the state of alcoholic solution, no precipitate is formed; but on evaporating the liquid,

there remains a slightly yellowish oil, which, indeed, separates as the alcohol evaporates; when this oil is shaken up with water, red iodide of mercury immediately separates out, and bromide of stibtriethyl remains in solution.

Iodide of stibtriethyl is soluble in water, alcohol, and ether.

Bromide of Stibtriethyl. $SbAe_3Br$.—Obtained by the action of bromide of mercury on iodide of stibtriethyl in alcoholic solution in the manner just mentioned—or better, by adding bromide of barium to the aqueous sulphate of stibtriethyl, as long as a precipitate is formed. The filtrate evaporated over the water-bath, and then in vacuo over oil of vitriol, exhibited traces of crystallization after a week.

Chloride of Stibtriethyl. $SbAe_3Cl$.—Obtained by decomposing the iodide with corrosive sublimate, the aqueous solutions of the two salts being mixed in exactly equal numbers of atoms; also by adding chloride of stibtriethyl and hydrogen to an aqueous solution of the oxide. Very soluble in water, and crystallizes only from highly concentrated solutions; no definite crystals were obtained. Forms a white, radiated mass, which rapidly absorbs water from the air.

On adding hydrochloric acid to the aqueous solution of this salt, the *acid chloride* $SbAe_3Cl,HCl$, separates in the form of a perfectly colourless liquid, containing 25·16 per cent. chlorine, the formula requiring 24·78 per cent.

The aqueous solution, mixed with bichloride of platinum, does not form any precipitate; but on evaporating the liquid, a dark-coloured oily substance is at length obtained, which, however, has not been further examined.

Nitrate of Stibtriethyl.—a. Neutral. $SbAe_3O,NO_5$.—Prepared by decomposing the iodide with nitrate of silver. On evaporating the filtrate, first, in the water-bath, and then over oil of vitriol in vacuo, the whole solidifies in a solid radiated mass, which dissolves very easily in water, but does not deliquesce in the air.

b. Acid. $SbAe_3O,HO,2NO_5$.—When the neutral nitrate is dissolved in dilute nitric acid, and the solution evaporated over the water-bath, the acid salt separates in oily drops, which solidify in a crystalline mass on cooling; and on dissolving this mass in water and evaporating, the acid salt is obtained in beautiful rhomboidal crystals, which dissolve readily in hot water. The salt thus obtained exhibits all the properties of the nitrate of stibethyl obtained by Löwig and Schweizer, in which they found 32·01 per cent. nitric acid; the above formula requires 31·67.

Acetate of Stibtriethyl.—When the solution of the oxide is saturated with acetic acid and the solution evaporated over the water-bath, there remains a thick syrupy residue, which does not crystallize, even after long standing in a warm place.

On the Stibamyls.*

By F. Berlé.

These compounds are formed by the action of iodide of amyl on antimonide of potassium. The latter substance (prepared by Löwig's process†) is finely pulverized, with addition of about half its bulk of dry sand; then introduced into glass flasks, in such quantity as to fill them to about two-thirds, and iodide of amyl added sufficient to moisten the mass throughout. After some time, and generally not till after the application of heat, a violent action takes place, attended with volatilization of the excess of iodide of amyl, which may be condensed by surmounting the flask with a distillation-tube. The flasks are then corked, their contents (a grey, pulverulent, coherent mass,) softened when cold with a small quantity of water, and emptied into a capacious cylinder, previously filled with carbonic acid gas. In this vessel, the product is repeatedly exhausted with ether; the ethereal solution, after it has become clear by standing, poured into a large flask filled with carbonic acid, and completely distilled off after addition of water or ether. The residue consists of *stibtriamyl*, protected from the action of the air by the water which is still present.

Pure *stibtriamyl* is a transparent, slightly yellowish liquid, very viscid below 20° C., more mobile at higher temperatures. Has a peculiar aromatic odour, and a bitter, somewhat metallic and very persistent taste. Sp. gr. = 1·1333 at 17° C. In contact with the air it fumes strongly, but does not take fire; it decomposes at the same time, with separation of a white powder. A drop of it placed on a piece of bibulous paper, and exposed to the air, becomes so strongly heated that the paper-fibre is charred. In presence of very small quantities (2 per cent) of amylic alcohol or iodide of amyl, stibtriamyl is also decomposed on exposure to the air, but without fuming or sensible rise of temperature. It is insoluble in water; sparingly soluble in absolute alcohol; very easily soluble in ether. Heated for eight days with iodide of amyl in a sealed glass tube, placed in the water-bath, it does not show any inclination to combine.

Stibtriamyl.		Calc.	Found.		
30 C . . .	180	52·63	53·55	52·56	51·66
33 H . . .	33	9·65	10·00	10·00	10·00
Sb . . .	129	37·72			
$(C_{10}H_{11})_3Sb$.	342	100·00			

* J. pr. Chem., lxv., 385; Ann. Ch. Pharm., xcvii., 316.
† Ann. Ch. Pharm., lxxv., 316.

If the stibtriamyl, prepared as above, is contaminated with free amylic alcohol (as when the iodide of amyl used in the preparation is impure) or with iodide of amyl, the following method may be adopted for the preparation of pure compounds. The impure stibtriamyl is dissolved in a mixture of ether and alcohol; bromine in alcoholic solution carefully added till its colour just begins to be permanent; then the bromide of stibtriamyl, precipitated by addition of a large quantity of water; the bromide converted into oxide of stibtriamyl, by means of silver-oxide suspended in alcohol; the resulting solution again precipitated by water; the separated oxide dissolved in hydrochloric acid and alcohol; and the pure chloride precipitated by another addition of water, and freed from a small quantity of water by continued heating to 100°, and the use of chloride of calcium.

Stibtriamyl combines with oxygen, iodine, &c., forming compounds, in which Berlé supposes 1 At. of the radical to be united with 2 At. of oxygen, &c.; the same view, in fact, as that proposed by Löwig for the compounds of stibethyl.*

Oxide of Stibtriamyl is produced by slow evaporation of an ethereal solution of stibtriamyl in contact with the air. There then remains a greyish yellow, very viscid, resinous mass, which becomes somewhat more fluid when heated, but readily decomposes at a higher temperature. Tastes and smells like stibtriamyl. Insoluble in water; sparingly soluble in hydrated alcohol and in ether; easily soluble in absolute alcohol. The alcoholic solution precipitates the oxides of the heavy metals from their salts. It dissolves readily in acids, and the resulting compounds are precipitated from their alcoholic solutions by water.

Chloride of Stibtriamyl.—Obtained by dissolving the oxide in hydrochloric acid, or by the method above described, is a yellowish, translucent liquid, viscid at ordinary, comparatively mobile at higher temperatures, heavier than water; dissolves in alcohol and ether. When precipitated from the alcoholic solution by water, it obstinately retains small portions of water and alcohol, from which it can only be freed by continued heating to 100°, and drying over chloride of calcium. Has a peculiar smell and taste, like the radical. Decomposes above 160°.

		Calc.	Found.	
Sb	129	31·23		
30 C	180	43·69	44·59	43·63
33 H	33	8·09	8·2	9·00
2 Cl	70	16·99	16·83	
$(C_{10}H_{11})_3Sb,Cl_2$	412	100·00		

* Chem. Soc. Qu. J., v., 69. For another view of the constitution of the compounds of metalliodal radicals, containing 1 At. metal to 3 At. of an alcohol-radical, see page 278 of this volume.

Iodide of Stibtriamyl is obtained by dissolving the oxide in hydriodic acid and precipitating by water, or by adding iodine to the radical as long as it is discolorized. Very much like the chloride. *Bromide of Stibtriamyl* is prepared in like manner, and exhibits similar properties.

Iodide.		Calc.	Found.	*Bromide.*		Calc.	Found.
Sb . . .	129	21·65		Sb	129	25·70	
30 C . . .	180	30·20	29·28	30 C	180	35·86	36·04
33 H . . .	33	5·54	6·10	33 H	33	6·57	6·75
2 I	252	42·61	40·00	2 Br	160	31·87	32·28
$(C_{10}H_{11})_3Sb,I_2$.	594	100·00		$(C_{10}H_{11})_3Sb,Br_2$.	502	100·00	

When chloride or iodide of stibtriamyl is mixed with an alcoholic solution of nitrate of silver, as long as a precipitate forms, and then filtered, the filtrate forms an emulsion, from which, after standing for some time in a warm place, two liquids separate, the upper being light, yellow and mobile, and the lower a deep brown-red oil. The upper layer, when slowly evaporated, yields slender white crystals grouped in stars; they may be purified by recrystallization from dilute alcohol. The dark red oil likewise dissolves on addition of a large quantity of hydrated alcohol, and the solution, after standing for some time, yields the same crystals. These crystals melt at about 20°; the fused mass does not dissolve in alcohol so readily as the crystals. This salt, the only crystallizable compound of stibtriamyl, is the *Nitrate of Stibtriamyl*, $(C_{10}H_{11})_3Sb_2,2NO_6$, (nitric acid by analysis 23·39 per cent.; by calculation 22·30); it is insoluble in water and ether, but dissolves in hydrated alcohol. Has a peculiar metallic taste.

By decomposing equivalent quantities of sulphate of silver and a haloid compound of stibtriamyl dissolved in alcohol, *Sulphate of Stibtriamyl* is obtained in solution. This salt was obtained only as an oily body, which yielded 18·03 per cent. sulphuric acid: the formula $C_{10}H_{11})_3Sb,2SO_4$ requires 18·26 per cent.

The white powder, formed by the action of the air upon stibtriamyl, is insoluble in ether, alcohol, and water; it does not dissolve in hydrochloric acid, but imperfectly in fuming nitric acid; slowly in aqua-regia. It remains unaltered even when strongly heated, not decomposing below a red heat. Berlé supposes it to be $(C_{10}H_{11})_3Sb,2SO_4 + 2SbO_3$. When sulphuretted hydrogen was passed for some time through this compound suspended in alcohol, a white powder immediately separated, which gradually assumed an orange colour, and then formed a pulpy mass, which could not be filtered. After addition of a large quantity of alcohol and ether, the liquid, when left to stand in a warm place, deposited an orange-red, flocculent precipitate, which after drying formed a brownish yellow powder, insoluble in alcohol, ether, and water; this powder decomposed at a very high

temperature, and took fire when fuming nitric acid was poured upon it. Berlé regards this compound as $(C_{10}H_{11})_3SbS_2+2SbS_3$ (it gave 18·38 per cent. sulphur, the formula requiring 17·59). A compound, supposed to be identical with this, is formed by passing sulphuretted hydrogen for some time through an alcoholic solution of oxide of stibtriamyl.

When the product of the action of iodide of amyl upon iodide of potassium, instead of being exhausted with ether, was distilled in an atmosphere of carbonic acid, a liquid passed over, which was freed from undecomposed iodide of amyl by distillation over antimonide of potassium. The liquid thus obtained gave off when heated to 80° C. a colourless gas, which had a peculiar odour; burnt with a bright flame, diffusing a white smoke of antimonic oxide; was not absorbed by water; but when left for some time in contact with it, deposited a white coating of antimony on the sides of the vessel. After the gas had been driven off, the liquid was greenish yellow, had a peculiar aromatic odour and bitter taste; was tolerably mobile, and heavier than water. It was insoluble in water, but miscible in all proportions with alcohol and ether. Exposed to the air, it does not fume or become heated; when set on fire, it burns with a very bright flame, diffusing a white fume of antimonic oxide; when heated in pure oxygen gas, it explodes with the greatest violence; fuming nitric acid decomposes it with considerable evolution of heat. This compound is *Stibbiamyl*.

		Calc.	Found.		
Sb . . .	129	47·6			
20 C	120	44·3	45·13	43·30	44·83
22 H	22	8·1	8·80	9·01	8·60
$(C_{10}H_{11})_2Sb$. .	271	100·0			

When an ethereal solution of stibbiamyl is left to evaporate in the air, the resulting oxide absorbs carbonic acid. The radical, heated for some time to 100° in a stream of dry carbonic acid, yielded a liquid similar in properties to the pure radical, but more viscid. This liquid gave 42·19 per cent. carbon, and is regarded by Berlé as $(C_{10}H_{11})_2SbO,CO_2$, this formula requiring 41·52 per cent. C. The haloid salts of stibbiamyl are gummy liquids; the sulphate and nitrate are precipitated from their alcoholic solutions by water in the form of gummy masses, which dry up to amorphous solids.

On Methyluramine and its Derivatives*.

By V. Dessaignes.

Two years ago, the author described† under the name *Methyluramine*, a strong base, produced by the action of mercuric oxide on creatine or creatinine.

$$\underbrace{2C_8H_9N_3O_4}_{\text{creatine.}} + 10\,O = \underbrace{2C_4H_7N_3,C_4H_2O_8}_{\text{oxalate of methyluramine.}} + 4CO_2 + 2HO.$$

$$\underbrace{2C_8H_7N_3O_2}_{\text{creatinine.}} + 10\,O + 2HO = 2C_4H_7N_3,C_4H_2O_8 + 4CO_2.$$

This base may be regarded as a compound formed from urea and methylamine, with elimination of 2 At. water:

$$C_4H_7N_3 + 2HO = C_2H_4N_2O_2 + C_2H_5N.$$

Creatine, on the other hand, may be regarded as glycolate of methyluramine *minus* water,—and sarcosine, its derivative, as an amide formed from glycolic acid and methylamine. If this view of the constitution of these bodies be correct, it must be possible to obtain methylamine from them. That such is the case, is shown by the following experiments.

The salts of methyluramine, heated with solution of potash, give off an abundance of alkaline vapours; and on absorbing these vapours by hydrochloric acid, evaporating the solution to dryness, and separating the greater part of the chloride of ammonium by means of absolute alcohol, an alcoholic solution is obtained, from which a salt crystallizes in shining laminæ; the platinum-salt prepared from this compound exhibits the composition of chloroplatinate of methylamine.

Creatine, heated with soda-lime, yields alkaline vapours, the platinum-salt of which, prepared as above, likewise exhibits the composition of chloroplatinate of methylamine.

Sarcosine, treated in the same manner, yields methylamine, which may also be obtained from it by the following reaction. When sulphate of sarcosine is dissolved in water, and heated with peroxide of lead, it is decomposed with brisk effervescence, the liquid assuming an alkaline reaction, and emitting a peculiar intoxicating odour: there is then formed a sulphate which may be decomposed by chloride of barium; and the resulting chloride, mixed with

* Compt. rend. xli, 1258; Ann. Ch. Pharm. xcvii, 339.
† Compt. rend. xxxviii, 839.

bichloride of platinum, yields chloroplatinate of methylamine in small hexagonal tables very pure and having a strong lustre.

Lastly, creatine oxidized by nitric acid with the aid of heat, yields ammonia and a base which Chevreul noticed but did not analyze. This base is also methylamine; but the platinum-salt obtained from it is difficult to free from the accompanying sal-ammoniac.

Peroxide of lead oxidizes creatine on addition of sulphuric acid, and on heating the mixture, the acid becomes almost saturated. The sulphate thus formed was converted into a hydrochlorate, and from this a platinum-salt was prepared which crystallized in beautiful orange-coloured prisms, and exhibited the composition of chloroplatinate of methyluramine. The crystallized oxalate effloresces at 100° C., and gives off 12·95 p.c. water; the base in the free state likewise exhibited all the properties of methyluramine; but the platinum-salt and the oxalate, even after repeated crystallizations, appeared to crystallize in forms different from those of the corresponding salts of methyluramine prepared with oxide of mercury.

When nitrous acid gas is passed through an aqueous solution of creatinine, the liquid effervesces, quickly turns brown, and then becomes turbid; and after a few hours, deposits an abundance of small indistinct and somewhat yellowish crystals, which become thick if left for some time in the liquid. These crystals are the nitrate of a new weak base, the salts of which are partially decomposed even by solution in water. A dilute solution of ammonia added to the acid liquid in sufficient quantity to saturate it, throws down a white amorphous powder insoluble in water. This base, after washing and drying, forms a light, coherent, friable mass, the powder of which is soft to the touch, and becomes electric by friction. It is tasteless. It dissolves in dilute acids when gently heated, and the solutions yield on cooling well crystallized and sparingly soluble salts.

Free Base.		Calc.	Found.
12 C	72	33·64	34·46
10 H	10	4·67	5·24
6 N	84	39·29	38·14
6 O	48	22·40	22·16
$C_{12}H_{10}N_6O_6$	214	100·00	100·00

The *hydrochlorate* forms short, deeply striated prisms, which give by analysis 25·18 p.c. C, 5·50 H, 27·40 N, and 17·95 Cl, agreeing nearly with the formula $2C_{12}H_{10}N_6O_6,3HCl+6Aq$. The *platinum-salt*, which is tolerably soluble, also forms large crystals, whose analysis gave 13·06 p.c. C, 2·83 H, 29·31 Cl, and 26·34 Pt, agreeing nearly with the formula $2C_{12}H_{10}N_6O_6,3HCl$,

$3PtCl_2+6Aq$. The formulæ of these salts are somewhat unusual, and stand in need of further verification. The following reaction, however, appears to confirm the formula assigned to the base:

When the base is heated to 100° C. with excess of hydrochloric acid, it is readily decomposed, with formation of oxalic acid, sal-ammoniac, and a body which crystallizes in long shining prisms or laminæ; dissolves slowly in cold, readily in hot water, and to a small amount in ether; has an unpleasant, almost metallic taste; is fusible; may be volatilized without decomposition; burns with flame and without residue; exerts a slight acid reaction upon litmus-paper, and does not precipitate the salts of lime, baryta, lead-oxide, cupric-oxide, zinc-oxide, or in dilute solution, chloride of mercury, or nitrate of silver. This body exhibits all the properties of the substance which Liebig* discovered as accompanying sarcosine in small quantity. To Liebig's description it is only necessary to add, that the substance precipitates nitrate of silver and mercurous nitrate in somewhat concentrated solutions. Its analysis gave 37·50 p.c. C, 3·12 H, and 21·87 N, agreeing very nearly with Liebig's formula $C_8H_4N_2O_6$.

The relations existing on the one hand, between creatinine and the insoluble base, and on the other hand between this base and the substance discovered by Liebig, may be expressed as follows:

$$\underbrace{2C_8H_7N_3O_2}_{\text{creatinine.}} + 14O = C_{12}H_{10}N_6O_6 + 4CO_2 + 4HO$$

$$\underbrace{C_{12}H_{10}N_6O_6}_{\text{insoluble base.}} + 8HO = C_8H_4N_2O_6 + 4NH_3 + C_4H_2O_8.$$

Creatine acted upon by nitrous acid, yields a small quantity of a white powder, whose identity with the base just described was established by its yielding the substance $C_8H_4N_2O_6$ when heated to 100° with hydrochloric acid. The same substance was likewise obtained when the acid mother-liquor from which the nitrate of the new base had crystallized was left to evaporate over lime within a bell-jar.

* Ann. Ch. Pharm. lxii, 317.

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On the Reciprocal Precipitations of the Metals.

By William Odling, M.B., L.R.C.P.,

SECRETARY TO THE CHEMICAL SOCIETY.

In a paper read at the Cheltenham meeting of the British Association, I observed that "when metallic cadmium is introduced into an acidulated or non-acidulated solution of chloride of copper, with, or more slowly without, ebullition, the whole of the copper is deposited in a red pulverulent state; but that when a piece of clean copper foil is immersed in a boiling, moderately concentrated, and slightly acidulated solution of chloride of cadmium, after some little time, a very brilliant coating of cadmium, of a white or yellowish-white colour, is precipitated upon the copper." This last decomposition being in very curious antagonism to Bergmann's view of single elective affinity, I was induced to make some further experiments upon the reciprocal precipitations of the metals. The results I have obtained form the subject of my present communication to this society.

Silver and Mercury.—The introduction of metallic mercury into a solution of nitrate of silver is followed by a beautiful growth of crystalline silver, constituting the well-known *Arbor Lunæ;* but when a piece of clean silver foil is immersed in a solution of mercurous nitrate, the foil becomes eventually covered with a semiliquid layer of amalgam, is rendered very brittle throughout, and, when heated in a tube, affords an abundant mercurial sublimate. The same result was obtained with pure metallic silver,

reduced from the chloride by carbonate of soda. Acidification and continued ebullition of the solution, facilitate, but are not by any means essential to, the deposition of the mercury. Thus it appears that, under circumstances of the greatest similarity, mercury will precipitate silver, and silver will precipitate mercury, from their respective nitric solutions. Moreover, silver, when boiled in an acidified solution of corrosive sublimate, becomes covered with a layer of calomel and metallic mercury, but the result is not so striking as that with the mercurous salt.

Silver and Copper.—When metallic copper is introduced into a solution of nitrate or sulphate of silver, or into a liquid turbid from the suspension of chloride of silver, a precipitate of silver takes place almost immediately. The deposit is generally pulverulent, but may be obtained from the sulphate and chloride as a brilliant metallic coating, provided the dilution be very considerable. Ebullition facilitates the deposition of silver from dilute solutions, but interferes with the appearance of the coating. When on the contrary a piece of silver foil, or of pure silver reduced from the chloride, is boiled in an acidulated and strong solution of sulphate of copper, after some time, the silver acquires a faint coating of metallic copper. When viewed in certain positions, the red colour of the copper is very apparent. When, however, the cupric coating is so thin as to be imperceptible to the eye, the presence of the metal may be evidenced by moistening the foil with ammonia, whereby the deep blue-coloured solution of cupramide is gradually developed; or better still, by heating the foil, when the redness of copper or its suboxide is frequently brought out with such intensity as entirely to conceal the colour of the silver. With a solution of nitrate of copper, the silver becomes discoloured, but there is no decided metallic precipitate. With solution of chloride of copper the results are most decided. The silver foil, or reduced silver, becomes almost immediately covered, even in the cold, with an opaque layer of a pale dull copper colour. By continued ebullition the colour of the coating becomes much deeper and less red. The deposit is capable of receiving a polish. It does not dissolve in cold hydrochloric acid, dilute or concentrated, but simply becomes more bright and red coloured. By boiling the coated foil, however, for some time, in strong hydrochloric acid, the copper disappears with the evolution of gas, and the silver remains coated with chloride of silver, which a slight rubbing readily removes. On gently heating the coated foil, a fine bronze colour is developed. That the coating is really

metallic copper, and not the suboxide, to the colour of which it sometimes most approximates, is, I consider, unquestionable. Its insolubility in cold hydrochloric acid, and its solubility in the boiling acid with the evolution of gas, leave no doubt upon the subject. I have satisfied myself by a great number of experiments, that pure metallic copper is soluble to a very manifest extent in boiling hydrochloric acid. There is, indeed, no difficulty in collecting considerable quantities of hydrogen generated by the reaction of hydrochloric acid and copper. I have employed wire, foil, gauze, electrotype copper, and copper reduced from the chloride by zinc, always with the same result. Moreover, pieces of electrotype copper and thin foil, after a very protracted ebullition, disappear completely in the acid, and that without any absorption of oxygen from the air. Throughout the experiment, hydrogen continues to be liberated, the dissolved copper exists in the state of subchloride, and the liquid consequently remains colourless.

Antimony and Copper.—The precipitation of antimony upon copper was, I believe, originally pointed out by Reinsch as giving rise to a possible fallacy in the use of his process for the detection of arsenic, and the re-action is now well known to chemists; but I find that, when pure metallic antimony is boiled with an acidulated solution of chloride of copper, the antimony receives a thin, but obvious coating of copper. The deposition of copper upon antimony takes place also in the cold, though much less quickly. In this case, the presence of the copper may be readily evinced by means of ammonia.

Bismuth and Copper.—The reciprocal precipitations of these two metals resemble very closely those of antimony and copper. The precipitate of copper upon pure bismuth, however, is not so manifest to the eye as is the cupric deposit upon antimony, owing probably to the greater want of contrast in the colours of the metals.

Copper and Tin.—When an acidulated solution of chloride of copper is boiled with metallic tin, the whole of the copper is deposited in a red or black pulverulent state. I find, on the other hand, that when clean copper is boiled in a moderately strong and rather acid solution of stannous chloride, the tin is deposited upon the copper in the form of a brilliant metallic coating of a somewhat darker colour than either the arsenical or antimonial coatings. In operating with dilute tin solutions, from which under any circumstances it is difficult to obtain a deposit, I have not found a

large excess of acid advisable. Reinsch alludes to a tarnish being produced upon copper when boiled in tin solutions.

Copper and Lead.—The introduction of a piece of clean lead into a solution of chloride of copper is followed by a precipitation of metallic copper in a red or black pulverulent state. But I find, contrary to the usual statements on the subject, that copper immersed in a boiling, saturated, and strongly acidified solution of chloride of lead, acquires, after some few minutes ebullition, a beautiful metallic coating of a somewhat bluish colour. When the liquid is but slightly acidified, the deposit is very faint, and amounts only to a tarnish.

Copper and Cadmium.—These results have been already alluded to. For the precipitation of cadmium upon copper, especially when the solution is somewhat weak, the acidification must be very slight, or be dispensed with altogether. When the precipitation takes place slowly, the gradual concealment of the colour of the copper by the deposit of cadmium gives rise to some very beautiful chromatic appearances. An equivalent of cadmium will completely abstract the copper from a solution of the neutral chloride, containing very much more than an equivalent of copper. In one experiment, only 72·75 per cent. of an equivalent of cadmium precipitated an equivalent of copper. Of course a portion only of the precipitated copper was in the metallic state. I have not succeeded in obtaining a *decided* deposit of cadmium upon pulverulent copper precipitated by cadmium or zinc. Moreover, it is difficult to obtain a coating upon electrotype copper until the metal has been fused and hammered. When a plate of cadmium and a plate of copper are immersed in dilute acid, the electric current proceeds, as is well known, from the copper to the cadmium, and when the two metals are immersed in a boiling solution of chloride of cadmium, the current maintains the same direction. During the passage of the current, it seems that the cadmium is deposited electrolytically, and that no solution of the copper takes place.

Tin and Lead.—When clean lead is introduced into an acidified and moderately strong solution of stannous chloride, with or without ebullition, a deposition of metallic tin in the form of a powder, or of minute crystals, is produced. The decomposition is, however, very incomplete. On the other hand, when a piece of tin foil, or pure tin, is introduced into an acidified, boiling solution of chloride of lead, a deposit of lead speedily takes place. So uniform is the coating, and so well marked its colour, that the tin

actually appears to have been converted into lead foil. Fischer alludes to the precipitation of lead from the acetate by means of tin, but his reaction is much less marked than that with the chloride.

Tin and Cadmium.—The introduction of cadmium into an acidified solution of stannous chloride is followed by the formation of the well-known tin tree or *Arbor Jovis*. But when a piece of tin foil, or pure tin, is immersed in a solution of chloride of cadmium, the latter metal is deposited upon the tin as a film having a somewhat iridescent appearance. By boiling a piece of tin in a strong solution of chloride of cadmium, a very abundant deposit of cadmium may be obtained.

Tin and Iron.—A piece of clean iron or steel, immersed in a boiling and tolerably concentrated solution of stannous chloride, acquires after some little time a pulverulent coating of tin; but when a piece of tin foil, or pure tin, is boiled in an acidulated solution of ferrous chloride, the tin receives a black-coloured coating, and becomes extremely brittle throughout. After being well washed with water, and boiled with hydrochloric acid, it yields a solution in which the presence of iron is abundantly manifest. The brittle residue, moreover, exerts a slight effect upon a delicate magnet. The reciprocal actions of tin with nickel and cobalt respectively, resemble perfectly the above-mentioned reactions with iron.

Lead and Cadmium.—Lead is readily precipitated by cadmium. From a solution of acetate of lead the *Arbor Saturnii* is produced with nearly as much facility by cadmium as by zinc. But when clean lead, pure or commercial, is boiled in a moderately concentrated solution of cadmic chloride, it speedily receives a brilliant, uniform, yellowish-white coating of metallic cadmium.

Cadmium and Iron.—A piece of clean iron or steel, when boiled in a solution of cadmic chloride, acquires a complete coating of metallic cadmium, having exactly the same appearance as when precipitated upon copper or lead. On the other hand, cadmium foil boiled in a solution of ferrous chloride receives a black coloured coating. This coated foil acts slightly on the magnet, and when washed with water and boiled with hydrochloric acid, yields a solution in which the presence of iron is at once evidenced by the usual reagents. Nickel and cobalt respectively reciprocate with cadmium in a manner precisely similar to that of iron. I find also that iron is precipitated to a very great extent by zinc; but I have not been able to reverse the experiment and precipitate zinc upon iron. In estimating iron by means of a standard solu-

tion of permanganate of potash, zinc is occasionally added to the iron solution, for the purpose of reducing the ferric to the ferrous salt. Unless care be taken to boil the liquid for some time with hydrochloric acid after the disappearance of the zinc, a very serious error may be introduced into the process by the abstraction of iron from the liquid.

From the above described experiments it appears that the reciprocal precipitation of the metals is a phenomenon of considerable generality; how, then, are the apparently antagonistic results to be explained? There can, I conceive, be no doubt whatever that, under certain specified conditions, the tendencies to the formation of some one particular compound are greater than the tendencies to the formation of some other analogous compound. Thus at a red heat, the tendencies to the formation of protoxide of lead are greater than the tendencies to the formation of the analogous protoxide of silver. Disregarding its etymology, we make use of the word affinity to express the tendencies which lead and oxygen have to unite with each other.* Admitting then to the full, that there are stronger tendencies or affinities leading to the production of one compound AB, than of another AC, we have to inquire how it is that AC is sometimes produced to the prejudice of AB.

From a variation in the conditions of the experiment.—It seems that the affinities leading to the production of any compound are not absolute, but variable, according to circumstances. Thus, at a red heat the tendencies to the production of oxide of iron or oxide of lead are greater than at ordinary temperatures. Now it is not improbable that the affinity of A for B shall in one set of conditions be greater than, and in another set of conditions be less than, that of A for C. But irrespective of any absolute variation in the powers of the different affinities, an alteration in the condition of the experiment brings other forces into play. Thus the well-known results of passing hydrogen over red-hot oxide of iron, and steam over red-hot metallic iron, have received an explanation from Mr. Graham to the effect—that in the

* In such a simple case as the above, the expressions affinity and chemical attraction are perfectly admissible. But when applied to more complex instances of combination, the phraseology becomes objectionable as necessarily representing to our minds some one or other speculative view concerning the constitution of the body under consideration. Thus in sulphate of barium, Ba^2SO^4, are we to speak of the affinity of baryta, Ba^2O, for sulphuric anhydride SO^3; or that of barium, Ba^2, for oxysulphide, SO^4; or that of peroxide of barium, Ba^2O^2, for sulphurous anhydride, SO^2; &c., &c. It is in this point of view that I take exception to the word affinity, which, however, it is scarcely possible to avoid employing.

former case, the diffusive tendency of steam into an atmosphere of hydrogen determines the reduction, and in the other, the diffusive tendency of hydrogen into an atmosphere of steam determines the oxidation of the iron. In a similar manner, when copper is boiled in a strong solution of chloride of cadmium, the diffusive or solvent force of chloride of copper may determine its formation. Water saturated with chloride of cadmium would be greedy of chloride of copper, and would yield the former metal in willing exchange for the latter. The solvent power of the cadmic solution for the cupric salt would exert a disposing affinity.

From the effect of mass.—The amount of evidence in favour of the general proposition by Berthollet, that "la quantité peut suppléer à la force de l'affinité pour produire un même degré de saturation," is now so great, as to render it almost indisputable. It is highly probable indeed that, were it not for interfering circumstances, if we had the electro-negative body A, and the metals B and C in excess, A would divide itself in the ratio of $\frac{x\,b}{x\,b + y\,c}$ to $\frac{y\,c}{x\,b + y\,c}$, where the tendency to form AB $= b$, the tendency to form AC $= c$, the amount of B $= x$, and the amount of C $= y$. It is obvious, however, that in many cases, superficies rather than mass will most influence the result. Mass may possibly exert a considerable effect in the cases where the precipitation of a metal from its acid solution is accompanied by a liberation of hydrogen. It is not improbable that the nascent hydrogen may preferably reduce the metal which was originally dissolved, in consequence of the greater quantity of the original, than of the subsequently formed salt. I find also that when a piece of clean iron is boiled in a solution of cadmic chloride containing a little cupric chloride as an impurity, copper and cadmium are simultaneously precipitated upon the iron which thus becomes coated with a species of brass. The precipitation of cadmium, however, despite its superior affinity, takes place to a very much greater extent than does the precipitation of copper, in consequence, I believe, of its superior mass. With a strong solution of cadmium the whole of the copper is not precipitated by iron, even after a somewhat protracted ebullition. Copper may, however, be readily removed from a dilute solution of cadmium, by agitating it with clean iron in the cold.

As a result of double decomposition from homogeneous affinity.—The propriety of representing chlorine, hydrogen, and the metals,

as binary molecules Cl Cl, H H, M M, respectively, as advocated by Brodie, Laurent, Gerhardt, and others, appears to receive confirmation from the phenomena of the mutual precipitation of the metals. By considering the precipitation of one metal upon another as an instance, not of single, but of double decomposition, I was enabled to explain several of the results I have already described. But, curiously enough, I find, not only that my explanation has been in its general nature anticipated by Berthollet, but that our modern notion of the homogeneous affinity of Cu for Cu, Hg for Hg, &c., is described by the same author in unmistakeable language. In accordance with these views, the precipitation of cadmium upon copper may be represented by the equation Cu Cu + Cd Cl = Cu Cd + Cu Cl, and the decomposition be determined by the circumstance that, in the conditions of the experiment, the sum of the affinities of Cu for Cd, and of Cu for Cl exceeds that of the affinities of Cu for Cu and Cd for Cl. Is there, however, any proof that a cadmide of copper is really formed? We know that an alloy differs greatly from a mixture of two metals, in the phenomena of its solution in acids. Thus an alloy of silver and platinum dissolves in nitric acid; but with the two metals in contact or mixture, there is an electric current generated; the silver is dissolved, and the platinum is left. An alloy of zinc and copper dissolves in hydrochloric acid; but with the two metals in contact or mixture, there is an electric current generated; the zinc is dissolved, and the copper remains. The solubility of pure copper in hydrochloric acid, to which I have before adverted, is not opposed to this result. Iron by itself is readily soluble in hydrochloric acid, but is not so in the presence of zinc. Now I find that a piece of copper coated with cadmium, and a coil of copper and cadmium foils rolled up together, behave very differently when treated with hydrochloric acid. Hydrochloric acid of the ordinary strength was diluted with a third of its volume of water and two equal portions boiled. Into one of the boiling liquids was immersed the compound coil, and into the other the coated foil. In both cases there was a considerable evolution of hydrogen, greater, however, with the coil than with the foil. The liquid in which the coil was immersed remained perfectly colourless, and even after a lapse of several hours had not dissolved a trace of copper. The liquid in which the coated foil was immersed became immediately green, and long before the cadmium had disappeared, contained copper in very considerable quantities, thus proving that the metallic deposit

partook of the characters of an alloy. In this case the solution probably took place according to the equation

$$\begin{aligned} &Cu\,Cd + H\;\;Cl + H\;\;Cl = \\ &H\;\;H\;\; + Cu\,Cl + Cd\,Cl. \end{aligned}$$

It might possibly have been

$$\begin{aligned} &Cu^2\,Cd + H\;\;Cl + H\;\;Cl = \\ &H\;\;H\;\; + Cu^2\,Cl + Cd\,Cl; \end{aligned}$$

but I am inclined to think from the instantaneous development of the green colour, in circumstances where an absorption of oxygen would have been difficult, that the former equation is correct. If the precipitation of one metal upon another be really due in great measure, as I believe it to be, to the affinity of the one metal for the other, the general result that I have arrived at, namely, that if the metal A can precipitate the metal B, the metal B will also precipitate the metal A, is sufficiently accounted for. This reciprocity, of course, will not be manifested when the tendency to form the salt of the one metal is very much greater than the tendency to form the salt of the other metal.

Note on the purity of the metals employed in the above-described experiments.

The pure silver was reduced from chloride of silver by fusion with carbonate of soda. The pure copper was precipitated electrolytically, upon a copper surface, by the current of a Daniell's cell. To obtain pure bismuth, nitrate of bismuth, after several crystallizations, was ignited, and the heated oxide reduced in a bulb-tube by a current of hydrogen gas. The hydrogen, prepared from the reaction of zinc and sulphuric acid, was passed successively through a solution of nitrate of silver, through a solution of hydrate of potash, and through oil of vitriol. 33·230 grains of oxide of bismuth, lost 3·445 grains. This result corresponds very closely with that obtained by Gmelin:—

		Calculated.	Lagerhjelm.	Gmelin.	Odling.
Bi . .	213	89·87	89·863	89·67	89·64
O . .	24	10·13	10·137	10·33	10·36

The pure lead was obtained from re-crystallized nitrate of lead. The salt was ignited and fused before the blowpipe with carbonate of soda. The pure tin was obtained electrolytically by immersing a bar of tin into two strata of liquid, the lower being a solution of crystallized stannous chloride, the upper being acidulated water. The pure antimony was obtained by incinerating re-crystallized tartar-emetic with carbonate of soda. The cadmium foil came into my hands as such. In its solution I was unable to detect the presence of zinc, or, with the exception of a very minute trace of iron, any other metal. The iron was employed only in the forms of commercial rolled iron and hard steel.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 3, 1856.

Dr. W. A. Miller, President, in the Chair.

The following donations were announced:—

"The Pharmaceutical Journal:" from the Editor.

"The American Journal of Science:" from the Editors.

"The Journal of the Franklin Institute:" from the Institute.

"The Canadian Journal of Industry and Science:" from the Editor.

"The Proceedings of the Royal Society:" from the Society.

"The Transactions and Proceedings of the Royal Society of Edinburgh:" from the Society.

"Memoirs of the Manchester Philosophical Society:" from the Society.

"Notes of Meetings and List of Members of the Royal Institution:" from the Institution.

"On Food, by Dr. Marcet:" from the Author.

Richard V. Tuson, Esq., of St. Bartholomew's Hospital, was elected a Fellow of the Society.

The following papers were read:—

"On the Reciprocal Precipitations of the Metals:" by W. Odling, M.B.

"On a new Series of Organo-thionic Acids:" by John T. Hobson.

November 17, 1856.

Dr. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced:—

"Proceedings of the Liverpool Literary and Philosophical Society:" from the Society.
"The Journal of the Franklin Institute:" from the Institute.
"The Journal of the Society of Arts:" from the Society.

The following papers were read:—

"On a new Volumetric Method for the determination of Copper:" by E. O. Brown.
"On the Action of Light upon Chloride of Silver:" by Frederick Guthrie, B.A., Ph.D.

December 1, 1856.

Dr. WILLIAMSON, Vice-President, in the Chair.

The following donations were announced:—

"The American Journal of Science:" from the Editors.
"The Journal of the Society of Arts:" from the Society.
"The Journal of the Franklin Institute:" from the Institute.
"The Pharmaceutical Journal:" from the Editor.

William Baker, Esq., Lead Works, Sheffield, was elected a Fellow of the Society.

The following papers were read:—

"On Compounds obtained by the action of Anhydrous Sulphuric Acid on the Chlorides of Hydrogen, Ethyl, and Methyl:" by R. Williamson.
"Note on the Action of Bichloride of Carbon on Ethylate of Potash:" by F. B. Lockwood.
"On some Thermo-electrical Properties of the metals Bismuth and Antimony, when used as single elements:" by Richard Adie.

December 15, 1856.

Dr. W. A. Miller, President, in the Chair.

The following gentlemen were elected Fellows of the Society:—

William Wallace, Esq., Andersonian Institution, Glasgow.
W. H. Perkin, Esq., Royal College of Chemistry.
John Horsley, Esq., Cheltenham.
John Hodgson Jones, Esq., 1, Poets' Corner, Westminster.
Charles Lowe, Esq., Halifax.

The following papers were read:

"On the Saponification of Resin:" by A. G. Anderson.

"On a Compound obtained by the action of fuming Sulphuric Acid on Chloride of Phenyl:" by L. Hutchings.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1856.

A.

Absorption.—Absorptiometric researches: by *L. Carius*. Ann. Ch. Phys. [3] xlvii. 418.

—— Law of absorption for ammoniacal gas: by *L. Carius*. Ann. Ch. Pharm. xcix. 129.

Acetal.—Researches on acetal and on the glycols: by *A. Wurtz*. Compt. rend. xliii. 478; Ann. Ch. Phys. [3] xlviii. 370; Ann. Ch. Pharm. c. 110.

Acetates.—On crystallised acetate of magnesia: by *C. v. Hauer*. J. pr. Chem. lxvi. 248; Chem. Gaz. 1856, 61.

—— Action of chloride of sulphur on acetate of soda: by *W. Heintz*. Pogg. Ann. xcviii. 458.

Acetylamine.—On acetylamine: by *J. Natanson*. Ann. Ch. Pharm. xcviii. 291; Ann. Ch. Phys. [3] xlviii. 111; Chem. Gaz. 1856, 303.

Acid, Acetic.—On the acidimitry of acetic acid: by *E. C. Nicholson* and *D. S. Price*. Chem. Gaz. 1856, 30.

Acid, Alloxanic.—On alloxanic acid: by *G. Städeler*. Ann. Ch. Pharm. xcvii. 120; Chem. Gaz. 1856, 73.

Acid, Anilotic.—On anilotic acid: by *R. Piria*. Ann. Ch. Pharm. xcvii. 253; Chem. Gaz. 1856, 169.

Acid, Amylophosphoric.—See *Amyl*.

Acid, Anisoic.—On anisoic acid: by *H. Limpricht*. Ann. Ch. Pharm. xcvii. 364; Chem. Soc. Qu. J. ix. 186; Ann. Ch. Phys. [3] xlviii. 117; Chem. Gaz. 1856, 167.

Acid, Arachinic.—On arachinic acid: by *H. Scheven* and *A. Gössmann*. Ann. Ch. Pharm. xcvii. 257; Ann. Ch. Phys. [3] xlvii. 382; Chem. Gaz. 1856, 181.

Acid, Arsenic.—See *Arsenic.*

Acid, Benzamic.—Preparation of benzamic acid; by *H. Limpricht.* Ann. Ch. Pharm. xcix. 118; Chem. Soc. Qu. J. ix. 264; Chem. Gaz. 1856, 330.

Acid, Boracic.—Extraction of boracic acid from the boraciferous lake of Monterotondo and the neighbouring soils: by *H. Duval.* Ann. Ch. Phys. [3] xlvi. 363.

—— Note on the production of boracic acid in Tuscany (conclusion): by *M. Péchiney-Rangot.* J. Pharm. [3] xxix. 16.

—— On the boracic acid fumeroles of Monte Cerboli, in Tuscany: by *C. Schmidt.* Ann. Ch. Pharm. xcviii. 273.

—— On the quantitative estimation of boracic acid: by *A. Stromeyer.* Ann. Ch. Pharm. c. 82.

Acid, Carbonic.—Fourth Note on the influence of light on the formation of carbonic acid in animals: by *J. Moleschott.* Compt. rend. xli. 961.

—— New experiments on the action of carbonic acid on the vegetable alkalis, alumina, sesquioxide of iron, and sesquioxide of chromium: by *M. Langlois.* Ann. Ch. Phys. [3] xlviii. 502.

—— New process for estimating carbonic acid in mineral waters, with considerations on the constitution of the Vichy waters: by *H. Buignet.* J. Pharm. [3] xxx. 321.

—— On the production of carbonic acid by the soil, by organic matters, and by manure: by *J. B. Cornwinder.* Ann. Ch. Phys. [3] xlviii. 179.

Acid, Caryophyllic.—On caryophyllic acid (*Nelkensäure*): by *L. Chiozza.* Ann. Ch. Pharm. xcix. 240.

Acid, Chrysophanic.—On chrysophanic acid, and on the constituents of the horse-chestnut: by *F. v. Rochleder.* J. pr. Chem. lxvi. 246; Ann. Ch. Phys. [3] xlvi. 373.

Acid, Cinnamic.—On the quantity of cinnamic acid which may be obtained from liquid storax. J. pr. Chem. lxvi. 187.

—— On the artificial preparation of cinnamic acid: by *C. Bertagnini.* Ann. Ch. Pharm. c. 125.

Acid, Citric.—On the constitution of citric acid: by *L. Pebal.* Ann. Ch. Pharm. xcviii. 67; Ann. Ch. Phys. [3] xlvii. 377.

Acid, Formic.—Researches on the relations between carbonic oxide and formic acid: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 477.

—— Transformation of carbonic oxide into formic acid: by *M. Berthelot.* Compt. rend. xli. 955; Ann. Ch. Pharm. xcvii. 125; Chem. Gaz. 1856, 9; Chem. Soc. Qu. J. ix. 182.

—— New method of preparing formic acid: by *M. Berthelot.* Compt. rend. xlii. 447; Ann. Ch. Pharm. xcviii. 139; Chem. Soc. Qu. J. ix. 182.

Acid, Gallic.—On the conversion of gallic into tannic acid in extracts of tannin: by *F. C. Calvert.* J. Pharm. [3] xxx. 31.

—— Preservation of solution of gallic acid: by *G. C. Lloyd.* N. Repert. Pharm. iv. 509; Pharm. J. Trans. xvi. 223.

Acid, Hippuric.—On the action of chloride of zinc on hippuric acid: by *A. Gössmann.* Ann. Ch. Pharm. c. 69.

Acid, Hippuric.—On the absence of hippuric acid in horse-urine: by *M. Roussin.* Compt. rend. xlii. 583; J. Pharm. [3] xxix. 263.

Acid, Hydriodic.—Action of hydriodic acid on silver: by *H. Sainte-Claire Deville.* Compt. rend. xlii. 894.

Acid, Hydrocyanic.—Preparation of hydrocyanic acid. Pharm. J. Trans. xv. 429.

Acid, Hydrobromic.—Decomposition of hydrobromic acid by aqueous potash and by mercury: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 492; J. Pharm. [3] xxix. 333.

Acid, Hydrochloric.—On the substitution of native sulphate of magnesia for sulphuric acid in the preparation of sulphate of soda and hydrochloric acid: by *R. de Luna.* Ann. Ch. Phys. [3] xlvii. 176.

—— Influence of hydrochloric acid on the precipitation of metals by sulphuretted hydrogen: by *M. Martin.* J. pr. Chem. lxvii. 371; Chem. Gaz. 1856, 311.

—— Note on the solubility of sulphate of baryta in hydrochloric acid: by *H. M. Noad.* Chem. Soc. Qu. J. ix. 15.

Acid, Hypogæic.—On some decomposition-products of hypogæic acid: by *G. C. Caldwell* and *A. Gössmann.* Ann. Ch. Pharm. xcix. 305.

Acid, Insolinic.—On insolinic acid: by *A. W. Hofmann.* Phil. Trans. 1856; Proc. Roy. Soc. viii. 1; Chem. Gaz., 1856, 17; Phil. Mag. [4] xii. 146; Ann. Ch. Pharm. xcvii. 197; Chem. Soc. Qu. J. ix. 210.

Acid, Methionic.—On methionic acid: by *A. Strecker.* Ann. Ch. Pharm. c. 199.

Acid, Nitric.—Researches on the formation of nitric acid: by *S. de Luca.* Compt. rend. xli. 1251; Chem. Gaz. 1856, 77.

—— Contributions to the history of nitric acid, with especial reference to the valuation of nitre: by *F. A. Abel* and *C. L. Bloxam.* Chem. Soc. Qu. J. ix. 37.

—— On the action of nitric acid upon alcohol at ordinary temperatures: by *H. Debus.* Phil. Mag. [4] xii. 361.

—— On various tests for nitric acid: by *C. Brame.* Compt. rend. xliii. 33.

—— On the detection of nitric acid in the air: by *M. Kletzinsky.* Chem. Gaz. 1856, 247.

—— Researches on the formation of nitric acid: by *S. De Luca.* Ann. Ch. Phys. [3] xlvi. 360; Compt. rend. xliii. 865.

Acid, Nitrohæmatic.—Identity of nitrohæmatic and picramic acids: by *A. Girard.* Compt. rend xlii. 59; Chem. Gaz. 1856, 90.

Acid, Oxalic.—On some reactions of oxalic acid: by *J. W. Slater.* Chem. Gaz. 1856, 130.

—— On a peculiar behaviour of oxalic acid with sesquioxide of iron: by *C. F. Schönbein.* J. pr. Chem. lxvi. 275.

Acid, Oxalovinic.—Formation of formiate of ethyl from oxalovinic acid: by *A. H. Church.* Phil. Mag. [4] xi. 527; Ann. Ch. Pharm. c. 256.

Acid, Oxyphenic.—On the supposed identity of oxyphenic acid with colourless hydrochinone: by *R. Wagner.* J. pr. Chem. lxvii. 490.

—— On the presence of oxyphenic acid in wood-vinegar: by *M. Buchner.* Ann. Ch. Phys. [3] xlvi. 377.

Acid, Palmitic.—On the action of potash-lime on palmitic acid, and on the nature of crude ethal: by *W. Heintz.* Ann. Ch. Pharm, xcvii. 271; Chem. Gaz. 1856, 222.

Acid, Phosphomolybdic.—See *Molybdenum.*

Acid, Phosphoric.—On molybdate of ammonia as a test for phosphoric acid: by *M. Bechamp.* J. Pharm. [3] xxix. 15.

—— On the quantitative estimation of phosphoric acid: by *W. Reissig.* Ann. Ch. Pharm. xcviii. 339; Chem. Gaz. 1856, 297.

—— On a new method of determining phosphoric acid: by *W. Knop.* Chem. Gaz. 1856, 435, 467.

Acid, Picric.—On the therapeutic employment of picric or carbazotic acid, and on its property of colouring the skin: by *MM. Calvert* and *Moffat.* Compt. rend. xliii. 104; Chem. Gaz. 1856, 384; Pharm. J. Trans. xiv. 167; J. Pharm. [3] xxx. 35.

—— On the detection of picric acid in beer: by *J. Pohl.* J. Pharm. [3] xxix. 465.

—— On the decoloration of silk and wool dyed with picric acid: by *C. Pugh.* Chem. Gaz. 1856, 297.

Acid, Rutic.—On rutic acid and quercitrin: by *H. Hlasiwetz.* Wien. Akad. Ber. xvii. 375; Chem. Gaz. 1856, 106; J. pr. Chem. lxvii. 97.

Acid, Salicyluric.—On salicyluric acid: by *C. Bertagnini.* Il Nuovo Cimento i. 363; Ann. Ch. Phys. [3] xlvii. 178.

Acid, Succinic.—On the preparation of succinic acid from malate of lime: by *E. J. Kohl.* Arch. Pharm. cxxxiv. 257; Chem. Gaz. 1856, 113.

Acid, Sulphuric.—On the action of sulphuric acid on the amides and nitriles, with remarks on the formation of the conjugate sulpho-acids: by *G. B. Buckton* and *A. W. Hofmann.* Phil. Trans. 1856; Chem. Soc. Qu. J. ix. 241; Proc. Roy. Soc. vii. 544; viii. 158; Chem. Gaz., 1856, 58.

—— On the action of nitric oxide gas on anhydrous sulphuric acid: by *A. Bruning.* Ann. Ch. Pharm. xcviii. 377; Chem. Gaz. 1856, 301.

—— Deposition of arsenious acid in commercial oil of vitriol. By *J. Cameron.* Chem. Gaz. 1856, 75.

—— On an improved method of manufacturing artificial soda and sulphuric acid: by *E. Kopp.* Ann. Ch. Phys. [3] xlviii. 81.

—— Processes for obtaining sulphate of soda, soda and sulphuric acid: by *L. Margueritte.* Chem. Gaz. 1856, 51.

—— On the preparation of chemically pure sulphuric acid: by *F. Vorwerk.* Chem. Gaz. 1856, 436.

Acid, Tannic.—On the nature of the tannic acids: by *F. Rochleder.* Wien. Akad. Ber. xviii. 3; Chem. Gaz. 1856, 366; J. pr. Chem. lxviii. 405.

Acid Tartaric.—Note on tartaric acid; by *M. Dubrunfaut.* Compt. rend. xlii. 192.

Acid, Thioformic.—On thioformic acid: by *H. Limpricht.* Ann. Ch. Pharm. xcvii. 361; Chem. Soc. Qu. J. ix. 184; Ann. Ch. Phys. [3] xlviii, 117; Chem. Gaz. 1856, 224.

Acid, Uric.—On the decomposition of uric acid in the animal body: by *C. Neubauer.* Ann. Ch. Pharm. xcix. 206.

—— On the occurrence of inosite, uric acid, &c., in the animal body: by *A. Cloëtta.* Ann. Ch. Pharm. xcix. 289; Ann. Ch. Phys. [3] xlvi, 369; Chem. Gaz. 1856, 61.

Acid, Toluric.—On toluric acid: by *C. Kraut.* Ann. Ch. Pharm. xcviii. 360.

Acids.—On the action of pentachloride of phosphorus on the fixed acids which give rise to the formation of pyro-acids: by *L. Bodart.* Compt. rend. xliii. 391.

—— On the behaviour of certain acids in the animal organism: by *C. Bertagnini.* Ann. Ch. Pharm. xcvii. 248; Chem. Gaz. 1856, 161.

—— On the reduction of the nitric derivatives of the acids homologous with benzoic acid: by *M. Boullet.* Compt. rend. xliii. 399.

—— New acid extracted from a Mexican plant, and possibly available in dyeing: by *M. Ramon de la Sagra.* Compt. rend. xlii. 873.

—— On a new acid obtained by the oxidation of hydrate of oil of turpentine: by *J. Personne.* Ann. Ch. Pharm. c. 253; Compt. rend. xliii. 553; Chem. Gaz. 1856, 371.

—— The diluted acids of the pharmacopœias: by *Mr. Squire.* Pharm. J. Trans. xv. 394; also by *Mr. Giles*, ibid. 409.

—— Valuation of commercial acids: by *M. Violette.* Compt. rend. xliii. 1010.

Acids, Fatty.—On the physiological action of the compounds of oxide of copper with the fatty acids: by *W. Langenbeck* and *G. Staedeler.* Ann. Ch. Pharm. xcvii. 155.

Acids, Organic.—On a new series of organic acids containing nitrogen: by *E. Frankland.* Proc. Royal Soc. viii. 198; Ann. Ch. Pharm. xcix. 342.

—— On the conversion of organic acids into the corresponding aldehydes: by *R. Piria.* Ann. Ch. Pharm. c. 104.

—— On the action of chloride of sulphur on some salts of the organic acids: by *W. Heintz.* Berl. Akad. Ber. 1856, 263; Chem. Gaz. 1856, 327.

Acids, Volatile.—On the volatile acids produced in the fermentation of diabetic urine: by *C. Neubauer.* Ann. Ch. Pharm. xcvii. 129; J. Pharm. [3] xxix. 320.

Acid Vapours.—On a new mode of arresting the acid vapours which escape from the tall chimneys of chemical manufactories: by *C.* and *A. Tissier.* Compt. rend. xli. 1045; Chem. Gaz. 1856, 54.

Aconite.—On the distinctive characters of the roots of monkshood (*Aconitum napellus*) and horse-radish (*Cochlearia armoracia*): by *R. Bentley.* Pharm. J. Trans. xv. 449.

—— On poisoning by aconite: by *M. Kosmann.* J. Pharm. [3] xxix. 366.

Aconitine.—Toxicological and pharmaco-dynamical researches on veratrine: by *Dr. von Praag.* J. Pharm. [3] xxix. 56.

Adipocire.—On adipocire: by *C. Wetherill.* J. pr. Chem. xlviii. 26.

Affinity.—On circumstances modifying the action of chemical affinity: by *J. H. Gladstone.* Chem. Soc. Qu. J. ix. 54.

—— On chemical affinity, and the solubility of sulphate of baryta in certain acid liquors: by *F. C. Calvert.* Proc. Roy. Soc. vii. 532; Chem. Gaz. 1856, 55; Phil. Mag. [4] xi. 390.

—— On some special affinities. Memoirs on some new facts relating to iodide of silver, and the metallic fluorides: by *H. Ste.-Claire Deville.* Compt. rend. xliii. 970.

Agarics.—Chemical researches on poisonous agarics: by *M. Gobley.* J. Pharm. [3] xxix. 81.

Agaricus.—On the cause of the phosphorescence of *Agaricus olearius:* by *M. Fabre.* Pogg. Ann. xcvii. 335; Phil. Mag. [4] xi. 165.

Agriculture.—Experiments made with a view to determine the comparative value of peat and peat-charcoal for agricultural purposes: by *E. W. Davy.* Phil. Mag. [4] xi. 172.

—— Miscellaneous notices from the agriculturo-chemical laboratory at Göttingen: by *W. Wicke.* Ann. Ch. Pharm. xcvii. 344, 350:—

I.—On granat-guano.
II.—Analysis of two marls from the Lüneburg.
III.—On the physiology of *Chrysomela ænea.*
IV.—Analysis of the ash of *Equisetum hiemale.*
V.—Analysis of the egg-shell of the ostrich.

Air.—Composition of the air enclosed within the fruit of the bladder senna (*Colutea arborescens*): by *M. Baudrimont.* Compt. rend. xli. 178; J. pr. Chem. lxvii. 188.

—— Determination of the weight of a given bulk of air: by *Dr. Seller.* Proc. Roy. Soc. Edinb. iii. 368.

—— On Regnault's determination of the weight of a litre of air, and on the density of water at O°C.: by *R. Kohlrausch.* Pogg. Ann. xcviii. 178.

—— On the supposed existence of iodine, and detection of nitric acid in the air: by *M. Kletzinsky.* Chem. Gaz. 1856, 247.

—— Pump.—On certain modifications of the form of the new double-acting air-pump with a single cylinder: by *T. Tate.* Phil. Mag. [4] xi. 364.

Albumin.—On the preparation of hæmatosin and albumin for technical purposes: by *J. Pillans.* Polyt. J. cxl. 298; Chem. Gaz. 1856, 390.

Albuminoid substances.—Extract from a thesis on albuminoid substances, and their transformation into urea: by *A. Béchamp.* Ann. Ch. Phys. [3] xlviii. 348.

Alcohol.—Preparation of alcohol of 40°: by *E. Fegneux.* J. Pharm. [3] xxix. 58.

—— On alcohol from colchicum: by *M. Comar.* J. Pharm. [3] xxix. 47.

—— Preparation of an alcoholic liquor from the stems of Jerusalem artichoke (*Helianthus tuberosus*): by *M. Decharmes.* Compt. rend. xlii. 438.

Alcohol.—On the action of nitric acid upon alcohol at common temperatures: by *H. Debus*. Phil. Mag. [4] xii. 361.

—— On the incandescence of metal wires in alcoholic vapour: by *H. Reinsch*. Phil. Mag. [4] xi. 246.

—— On small vertical movements in mixtures of alcohol and volatile liquids: by *P. Harting*. Pogg. Ann. xcvii. 50.

—— Note on a compound of baryta and alcohol: by *M. Berthelot*. Ann. Ch. Phys. [3] xlvi. 180; Ann. Ch. Pharm. xcviii. 180; Chem. Gaz. 1856, 227.

—— On some products of the oxidation of alcohol: by *H. Debus*. Ann. Ch. Pharm. c. 1.

—— Purification of alcohol. Pharm. J. Trans. xvi. 330.

Alcohols.—On a new class of alcohols: by *A. Cahours* and *A. W. Hofmann*. Proc. Roy. Soc. viii. 33; Chem. Gaz. 1856, 156; Phil. Mag. [4] xii. 309; Compt. rend. xl. 217; Pharm. J. Trans. xv. 519.

—— On anisic alcohol: by *S. Cannizzaro* and *C. Bertagnini*. Ann. Ch. Pharm. xcviii. 188; Chem. Soc. Qu. J. ix. 190; Ann. Ch. Phys. [3] xlvii. 285; Chem. Gaz. 1856, 368.

—— On a new alcohol extracted from a particular kind of whale-oil: by *M. Scharling*. Ann. Ch. Pharm. xcvi. 263; J. Pharm. [3] xxix. 76.

Aldehyde.—On the crystalline form of aldehyde-ammonia: by *C. Rammelsberg*. Pogg. Ann. xcvi. 625; also by *C. Heusser*, ibid. xcix. 171.

—— A compound formed from aldehyde-ammonia and chloride of benzoyl: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 119; Chem. Soc. Qu. J. ix. 265.

Aldehydes.—On a new mode of formation of hydride of benzoyle, and on the chemical constitution of the aldehydes: by *H. Kolbe*. Ann. Ch. Pharm. xcviii. 344; Chem. Soc. Qu. J. ix. 266.

—— Preparation of aldehydes from the acids $C_nH_nO_4$: by *H. Limpricht*. Ann. Ch. Pharm. xcvii. 368; Chem. Soc. Qu. J. ix. 87; Ann. Ch. Phys. [3] xlviii. 118.

—— On the transformation of certain acids into the corresponding aldehydes: by *R. Piria*. Il nuovo Cimento, iii. 126. Ann. Ch. Phys. [3] xlvii. 113; Ann. Ch. Pharm. c. 104.

—— On the formation of caprylic aldehyde: by *J. Bouis*. Ann. Ch. Phys. [3] xlviii. 99; Ann. Ch. Pharm. xcvii. 34.

Alkalis.—Action of alkalis on sugar in the animal economy: by *M. Poggiale*. Compt. rend. xlii. 198.

—— Action of carbonic acid on the vegetable alkalis: by *M. Langlois*. Ann. Ch. Phys. [3] xlviii. 502.

Alkalies.—Improvements in the manufacture of alkalies and alkaline earths: (*R. A. Tilghman's* patent) Chem. Gaz. 1856, 359.

Alkaloïds.—On a new method of extracting the alkaloïds contained in nux vomica, without alcohol: by *J. Horsley*. Pharm. J. Trans. xvi. 179.

Alloy.—Analysis and preparation of an alloy for composition-files: by *A. Vogel*. N. Jahrb. Pharm. iv. 138; Chem. Gaz. 1856, 54.

Alloys—On some crystalline alloys: by *F. L. Sonnenschein.* J. pr. Chem. lxvii. 168.

—— The manufacture of alloys or combinations of metals. J. Fr. Inst. [3] xxxii. 191.

—— On the form of an alloy of bismuth: by *W. H. Miller;* with an analysis of the alloy: by *A. Dick.* Phil. Mag. [4] xii. 48.

Aloetine.—Researches on aloetine: by *E. Robiquet.* J. Pharm. [3] xxix. 241.

Aloine.—On aloine: by *T. R. Groves.* Pharm. J. Trans. xvi. 128.

Alum.—On the chemical characters of red wines to which alum has been added; and application of these characters to the detection of small quantities of this salt introduced into the wine: by *M. Lassaigne.* Compt. rend. xlii. 410; Chem. Gaz. 1856, 136.

Alumina.—On the preparation of alumina: by *C. v. Hauer.* Geol. Soc. Qu. J. xii. pt. 151.

—— Analysis of a mixture of alumina and sesquioxide of iron. J. Pharm. [3] xxix. 59.

—— Action of carbonic acid on alumina. Ann. Ch. Phys. [3] xlviii. 502.

Aluminium.—Supposed native occurrence of aluminium. Compt. rend. xli. 412; J. pr. Chem. lxvi. 470.

—— New mode of preparing aluminium and certain simple substances, metallic and non-metallic: by *H. Ste. Claire Deville.* Compt. rend. xli. 1053; Chem. Gaz. 1856, 32.

—— On the preparation of aluminium: by *C. Brunner.* Dingl. Polyt. J. cxl. 357; Chem. Gaz. 1856, 340; Pogg. Ann. xcviii. 488.

—— Preparation of aluminium on the large scale. Compt. rend. xliii. 712.

—— On the aluminium prepared in Paris. J. pr. Chem. lxvii, 493.

—— On the reduction of aluminium from cryolite: by *F. Wöhler.* Ann. Ch. Pharm. xcix. 255; Chem. Gaz. 1856, 381.

—— On the preparation of sodium and aluminium: by *H. Ste. Claire Deville.* Ann. Ch. Phys. [3] xlvi. 415.

—— Electric conductivity of aluminium. Pogg. Ann. xcvii. 643.

—— On the thermo-electrical position of aluminium: by *W. Thomson.* Pogg. Ann. xcix. 334. Also by *G. Gore.* Pharm. J. Trans. xv. 506.

—— Preparation and properties of fluoride of aluminium: by *H. Ste. Claire Deville.* Compt. rend. xlii. 49; Chem. Gaz. 1856, 101.

—— On the transformation of fluoride of aluminium and sodium into aluminate of soda: by *C. Tissier.* Compt. rend. xliii. 102; Chem. Gaz. 1856, 344.

—— On the alloys of aluminium: by *H. Debray.* Compt. rend. xliii. 925; Chem. Gaz. 1856, 463.

Allyl.—On allyl and the allylic ethers: by *MM. Berthelot* and *De Luca.* Ann. Ch. Phys. [3] xlviii. 286.

Amides.—On the action of sulphuric acid on the amides and nitriles: by *G. V. Buckton* and *A. W. Hofmann.* Phil. Trans. 1856; Chem. Soc. Qu. J. ix. 241; Proc. Roy. Soc. vii. 544; viii. 158; Chem. Gaz. 1856, 58, 305; Phil. Mag. [4] xi. 549; Ann. Ch. Phys. [3] xlvi. 366.

Amides.—On the formulæ of some amides and ureas, and on the possibility of the artificial formation of creatine and creatinine: by *C. Weltzien*. Ann. Ch. Pharm. c. 191.

—— Researches on the amides: by *C. Gerhardt* and *L. Chiozza*. Ann. Ch. Phys. [3] xlvi. 129.

Ammonia.—On the behaviour of iodide of mercury with ammonia: and on a new test for ammonia: by *J. Nessler*. Chem. Gaz. 1856, 446, 463.

—— On the preparation of gaseous ammonia: by *M. Vogel*. N. Repert. Pharm. iv. 244; J. Pharm. [3] xxviii, 485.

—— Preparation of ammonia. Pharm. J. Trans. xvi. 223.

—— On the presence of ammonia in certain mineral waters: by *M. Bouis*. Compt. rend. xlii. 1269.

—— Law of absorption for ammoniacal gas: by *L. Carius*. Ann. Ch. Pharm. xcix. 129.

—— On the double compounds of cyanogen with copper and ammonia: by *L. Hilkenkamp*. Ann. Ch. Pharm. xcvii. 218; Ann. Ch. Phys. [3] xlvii. 181.

—— On the ammoniacal hyposulphate of copper, and on the ammonia salts of metals in general: by *E. Schweizer*. J. pr. Chem. lxvii. 430.

—— A salt which gives off ammonia when treated with hydrochloric acid. Ann. Ch. Pharm. xcvii. 18.

—— Observations on the absorption of ammonia and nitrates by cryptogamic plants: by *A. B. Bineau*. Ann. Ch. Phys. [3] xlvi. 60.

—— On the oxidation of the constituents of ammonia by porous media, with some remarks on nitrifaction: by *C. F. Schönbein*. Phil. Mag. [4] xii. 457.

Ammonium.—On the ammonium-molecules of the metals: by *C. Weltzien*. Ann. Ch. Pharm. xcvii. 19, and c. 108. Also by *C. Claus*. ibid. xcviii. 317.

—— Volumetric determination of ammonia by means of silver: by *C. Mohr*. Ann. Ch. Pharm. xcix. 197.

Amulet.—Analysis of a Babylonian cylinder and amulet: by *J. Spiller*. Phil. Mag. [4] xi. 107.

Amyl.—Action of chloride of mercury on iodide of amyl: by *M. Schlagdenhauffen*. J. Pharm. [3] xxix. 247.

—— On amylophosphoric acid: by *F. Guthrie*. Chem. Soc. Qu. J. ix. 134; Ann. Ch. Pharm. xcix. 57.

—— On the stibamyls: by *F. Berlé*. Ann. Ch. Pharm. xcvii. 316; Chem. Soc. Qu. J. ix. 282; J. pr. Chem. lxv. 385; Chem. Gaz. 1856, 68.

—— On telluramyl and selenmethyl: by *F. Wöhler* and *J. Dean*. Ann. Ch. Pharm. xcvii. 1; Sill. Am. J. [2] xxi. 245.

Analysis.—Use of bicarbonate of baryta in analysis. J. pr Chem. lxvii. 10.

—— On the use of hyposulphite of soda in quantitative analysis: by *H. Vohl*. Ann. Ch. Pharm. xcvi. 237; J. Pharm. [3] xxix. 74.

Analysis, Volumetric.—New method of estimating chlorine in compounds: by *C. Mohr*. Ann. Ch. Pharm. xcvii. 335; Ann. Ch. Phys. [3] xlvii. 376; Chem. Gaz. 1856, 174.

Analysis, volumetric.—On the volumetric determination of ammonia, carbonic acid, alkaline and earthy carbonates, nitrogen, chlorates, iodates, bromates, nitrates, and salts of vegetable acids, by means of silver: by *D. Mohr.* Chem. Gaz. 1856, 406.

—— Volumetric determination of ammonia, alkaline and earthy carbonates, nitrogen, chlorates, iodates, bromates, nitrates, and salts of vegetable acids, by means of silver: by *C. Mohr.* Ann. Ch. Pharm. xcix. 197.

Annatto.—On the adulteration of annatto: by *A. H. Hassall.* Pharm. J. Trans. xv. 295, 323.

Aniline.—On the anilides of malic acid: by *A. E. Arppe.* J. pr. Chem. lxvii. 129.

Animal Substances.—Preservation of animal substances by the saturated aqueous solution of sulphate of zinc: by *M. Strauss-Durckheim.* Compt. rend. xlii. 808.

Antimony.—On the atomic weight of antimony: by *H. Rose.* Berl. Akad. Ber. 1856, 239; J. pr. Chem. lxviii. 372.

—— On the atomic weight of antimony: by *R. Schneider.* Pogg. Ann. xcvii. 293, 483; Chem. Gaz. 1856, 163; J. pr. Chem. lxviii. 115; Ann. Ch. Pharm. c. 120.

—— On the bursting of antimony precipitated by galvanic action: by *R. Böttger.* Pogg. Ann. xcvii. 333.

—— On a method of distinguishing arsenic spots from antimony: by *M. Schönbein.* J. Pharm. [3] xxix. 316.

—— On various tests for antimony: by *C. Brame.* Compt. rend. xliii. 33.

—— On the electrical relations of lead and antimony in various conducting liquids: by *G. Gore.* Pharm. J. Trans. xv. 413.

—— New method of assaying the sulphides of lead and antimony: by *A. Levol.* Ann. Ch. Phys. [3] xlvi. 472; Chem. Gaz. 1856, 353.

—— On antimonial vermilion: by *E. M. Plessy.* Chem. Gaz. 1856, 103.

—— On the precipitation of terchloride of antimony by water: by *E. Baudrimont.* Compt. rend. xlii. 863; Chem. Gaz. 1856, 242; J. Pharm. [3] xxix. 436.

—— On the formation of suboxide of antimony, and spontaneously inflammable antimoniuretted hydrogen, by the galvanic process: by *R. Böttger.* J. pr. Chem. lxviii. 372.

—— On two new crystalline compounds of zinc and antimony discovered by J. P. Cooke, jun.: by *A. Kenngott.* Pogg. Ann. xcvi. 584.

—— On the compounds of stibamyl: by *F. Berlé.* J. pr. Chem. lxv 385; Chem. Gaz. 1856, 68; Ann. Ch. Pharm. xcvii. 316; Chem. Soc. Qu. J. ix. 282.

—— On the compounds of stibethyl: by *W. Merck.* Ann. Ch. Pharm. xcvii. 329; Chem. Soc. Qu. J. ix. 278.

—— On stibethylium and its compounds: by *R. Löwig.* Ann. Ch. Pharm. xcvii. 329.

—— On the detection of antimony for medico-legal purposes: by *W. Odling.* Guy's Hospital Reports, [3] ii. 249.

Arachins.—On the arachins: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvii. 355.

Arsenic.—Action of the air upon alkaline arsenites: J. Pharm. [3] xxix. 262.

—— On the chemical composition of some varieties of arsenical pyrites and arsenide of iron: by *G. A. Behncke.* Pogg. Ann. xcviii. 184.

—— On the preparation and properties of arsenic acid: by *E. Kopp.* Ann. Ch. Phys. [3] xlviii. 106; Compt. rend. xlii. 1060; Chem. Gaz. 1856, 250.

—— Deposition of arsenious acid in commercial oil of vitriol: by *J. Cameron.* Chem. Gaz. 1856, 75.

—— On a method of distinguishing arsenic spots from antimony spots: by *M. Schönbein.* J. Pharm. [3] xxix. 316.

—— On molybdate of ammonia as a test for arsenic acid: by *A. Béchamp.* J. Pharm. [3] xxix. 15.

—— On various tests for arsenic: by *C. Brame.* Compt. rend. xliii. 33.

—— On the occasional use of arsenic in the steeping of grain: by *M. Boussingault.* Ann. Ch. Phys. [3] xlvi. 458.

Ash.—On a considerable amount of iron and manganese in the ash of a water-plant: by *E. v. Gorup-Besanez.* Ann. Ch. Pharm. c. 106.

Ashes.—Analyses of the ashes of malt: by *H. Scheven.* J. pr. Chem. lxvi. 315.

—— On the action of lixiviated ashes on fallow-land: by *A. Bobierre.* Compt. rend. xliii. 473.

—— New method of preparing ashes for analysis: by *H. Hlasiwetz.* Ann. Ch. Pharm. xcvii. 244.

Aspidium.—Analysis of the ash of the fronds of *Aspidium filix mas.* and *A. filix fœmina*: by *C. Struckmann.* Ann. Ch. Pharm. xcvii. 143.

Azobenzol.—On azobenzol and benzidine: by *A. Noble.* Ann. Ch. Pharm. xcviii. 253.

B.

Balsams.—Contributions to the chemical history of the balsams which occur in commerce: by *E. A. Scharling.* Ann. Ch. Pharm. xcvii. 68, 155; Ann. Ch. Phys. [3] xlvii. 385.

Barium.—On the iodides of barium and strontium: by *H. Croft.* Chem. Gaz. 1856, 125.

Bark.—On the bark of *Cail cedra* (*Khaya Senegalensis*): by *L. Soubeiran.* J. Pharm. [3] xxx. 122.

Barley.—On the growth of barley: by *H. Scheven.* J. pr. Chem. lxvii. 193.

Barometer.—Note on the construction of the barometer, and on the ebullition of mercury in vacuo: by *M. Taupenot.* Compt. rend. xlii. 1186.

Baryta.—Note on a compound of baryta and alchohol: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 180; Ann. Ch. Pharm. xcvii. 180; Chem. Gaz. 1856, 227.

Baryta.—On crystallised hydrate of baryta: by *F. Mohr*. Pharm. J. Trans. xvi. 309.

—— On the use of bicarbonate of baryta in analysis. J. pr. Chem. lxvii. 10.

—— Use of hydrate of baryta in softening calcareous waters: by *E. H. Durden*. Pharm. J. Trans. xv. 352.

—— On the solubility of sulphate of baryta in certain acid liquors: by *F. C. Calvert*. Proc. Roy. Soc. vii. 532; Chem. Gaz. 1856, 55.

—— Note on the solubility of sulphate of baryta in hydrochloric acid: by *H. M. Noad*. Chem. Soc. Qu. J. ix. 15.

—— On the solubility of sulphate of baryta in nitric acid: by *E. C. Nicholson* and *D. S. Price*. Phil. Mag. [4] xi. 169.

Bases Organic.—Researches on some new phosphuretted bases: by *A. Cahours* and *A. W. Hofmann*. Chem. Gaz. 1856, 10; Compt. rend. xliii. 1092.

Belladonna.—Iodine as an antidote for poisoning by belladonna. J. Pharm. xxix. 219.

Beet.—Researches on the distribution of nitrogenous matters in the several parts of the beet-plant: by *J. Pierre*. Compt. rend. xlii. 715.

—— Analysis of the residues of the defecation of beet-juice, and of the potashes of beet-molasses: by *E. Ducastel*. J. Pharm. [3] xxix. 292.

—— Preservation of beet-juice by means of lime: by *E. Maumené*. Compt. rend, xlii. 645.

Benzidine.—On azobenzol and benzidine: by *A. Noble*. Ann. Ch. Pharm. xcviii. 253.

Benzoates.—Action of chloride of sulphur on benzoate of soda: by *W. Heintz*. Pogg. Ann. xcviii. 458.

Benzol.—On benzol in coal-gas: by *R. Pitschke*. J. pr. Chem. lxvii. 415.

—— On some new colouring matters, derivatives of dinitrobenzol and dinitronaphthaline: by *A. H. Church* and *W. H. Perkin*. Chem. Soc. Qu. J. ix. 1.

Benzoyl.—On some benzoyl-compounds: by *Carl Voit*. Ann. Ch. Pharm. xcix. 100; Chem. Soc. Qu. J. ix. 268.

—— A compound formed from aldehyde-ammonia and chloride of benzoyl: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 119; Chem. Soc. Qu. J. ix. 265.

—— On sulphocyanide of benzoyl: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 117; Chem. Soc. Qu. J. ix. 264; Chem. Gaz. 1856, 351.

—— On a new mode of formation of hydride of benzoyl, and on the chemical constitution of the aldehydes: by *H. Kolbe*. Ann. Ch. Pharm. xcviii. 344; Chem. Soc. Qu. J. ix. 266.

Biformene.—Note on the derivatives of thymol, and on the preparation of biformene, a homolgue of marsh-gas: by *M. Lallemand*. Compt. rend. xliii. 375; report by *M. Bussy*, ibid. 459.

Bile.—Researches on the biliary secretion: by *M. Ore*. Compt. rend. xlii. 497.

Bile.—On the conversion of the acids of the bile into the biliary colouring matter: by *Frierichs* and *Städeler*. Chem. Gaz. 1856, 141.

—— Experimental researches on the functions of the mucous membrane of the gall-bladder, principally with reference to the conversion of hepatic into cystic bile: by *G. Kemp*. Proc. Roy. Soc. viii. 133.

—— Researches on the chemical nature and properties of the fatty matters contained in bile: by *M. Gobley*. J. Pharm. [3] xxx. 241.

—— Influence of the obliteration of the *vena porta* on the secretion of the bile, and on the glycogenic function of the liver: by *M. Ore*. Compt. rend. xliii. 463; Remarks by *M. Andral*, ibid. 467.

Bismuth.—Researches on bismuth and its compounds: by *R. Schneider*. Ann. Ch. Pharm. xcvii. 192.

—— On the deportment of bismuth during solidification: by *R. Schneider*. Phil. Mag. [4] xi. 18.

—— On a peculiar property of bismuth: by *R. Schneider*. J. pr. Chem. lxvi. 189; J. Pharm. [3] xxix. 237.

—— On the determination of bismuth by weight and volume: by *R. W. Pearson*. Phil. Mag. [4] xi. 204.

—— On the quantitative separation of bismuth by means of a solution of bichromate of potash: by *J. Löwe*. J. pr. Chem. lxvii. 464, 469.

—— On copper-bismuth-glance from *Wittichen*: by *R. Schneider*. Pogg. Ann. xcvii. 476; J. pr. Chem. lxvii. 205.

—— On the form of an alloy of bismuth: by *W. H. Miller*; with an analysis of the alloy: by *A. Dick*. Phil. Mag. [4] ii. 48.

—— On chloride of bismuth: by *H. Rose*. J. pr. Chem. lxvi. 251.

—— On the chromates of bismuth: by *J. Löwe*. J. pr. Chem. lxvii. 288, 463.

—— On the preparation of bisulphide of bismuth in the wet way: by *R. Schneider*. Pogg. Ann. xcvii. 480.

—— On teriodide of bismuth: by *R. Schneider*. Pogg. Ann. xcix. 470.

Bleaching.—Improvements in bleaching vegetable fibres (J. Jennings' patent). Chem. Gaz. 1856, 450.

Blood.—Chemical examination of the blood: by *J. Scherer*. Chem. Gaz. 1856, 295.

—— On the constitution of the blood of different vessels, particularly with reference to the amount of sugar contained in it: by *C. G. Lehmann*. J. pr. Chem. lxvii. 321.

—— Remarks on M. Lehmann's memoir on the detection of sugar in the blood of the *vena porta*; by *L. Figuier*. J. Pharm. [3] xxix. 96.

—— On the condition of the oxygen absorbed into the blood during respiration: by *G. Harley*. Proc. Roy. Soc. viii. 78; Chem. Gaz. 1856, 196.

—— Analysis of the blood of a woman who died after inhaling chloroform: by *M. Jackson*. Compt. rend. xlii. 411.

Blood.—Presence of fluorine in the blood: by *J. Nickles.* Compt. rend. xliii. 885.

—— Effects produced on the blood by different vegetable infusions: by *M. Le Clerc.* Compt. rend. xlii. 456, 690.

—— On the detection of blood and blood-spots in judicial investigations: by *H. Rose.* J. Pharm. [3] xxviii. 436.

—— On the detection of sugar in the blood of the *vena porta*: by *C. G. Lehmann.* J. Pharm. [3] xxviii. 449. Remarks by *C. Bernard*, ibid.; also by *L. Figuier*, ibid. xxix. 96.

Boiling Point.—See *Heat.*

Bones.—On the solubility of bones in water. Ann. Ch. Pharm. xcviii. 143; Chem. Gaz. 1856, 203.

—— Presence of vivianite in interred human bones: by *J. Nickles.* J. Pharm. [3] xxix. 94; Compt. rend. xli. 169.

—— On the superphosphate of decomposed bones: by *W. Wicke.* Ann. Ch. Pharm. xcix. 97; Chem. Gaz. 1856, 333.

Borates.—On borate of ethyl: by *H. Rose.* Pogg. Ann. xcviii. 245.

Boron.—Memoir on boron: by *F. Wöhler* and *H. Deville.* Compt. rend. xliii. 1088.

Brain.—Quantitative examination of the softened brain of a child: by *J. Schlossberger.* J. pr. Chem. lxviii. 59.

Bread.—On bread and its preparation: by *M. Mege-Mouries.* Compt. rend. xlii. 1122.

—— On bread made of a mixture of corn and rice: by *M. Girardin.* J. Pharm. [3] xxx. 101.

—— On the causes of an accidental colouring in bread: by *M. Poggiale.* J. Pharm. [3] xxx. 96.

—— On the examination of flour and bread: by *L. E. Rivot.* Compt. rend. xlii. 633; Ann. Ch. Phys. [3] xlvii. 50.

Bromates.—Volumetric determination of bromates by silver: by *C. Mohr.* Ann. Ch. Pharm. xcix. 197.

Bromine.—On the boiling points of analogous bromine and chlorine compounds: by *H. Kopp.* Ann. Ch. Pharm. xcviii. 265.

—— On the bromide of titanium: by *F. B. Duppa.* Proc. Roy. Soc. viii. 42; Chem. Gaz. 1856, 138; Phil. Mag. [4] xii. 232; Ann. Ch. Phys. [3] xlvii. 164—Remarks by H. Kopp, ibid. 160.

—— On the bromide of titanium: by *A. W. Hofmann.* Compt. rend. xlii. 352; Ann. Ch. Pharm. xcvii. 510.

Bronze.—Analysis of bronze: by *C. B. Hambly.* Chem. Gaz. 1856, 216.

—— Composition of the bronze of statuettes found at the Serapeum: by *M. Chevreul.* Compt. rend. xliii. 733. 989.

Brucine.—On the action of iodide of ethyl on brucine: by *Dr. Gunning.* J. pr. Chem. lxvii. 46.

Building Materials.—On the materials adapted for marine buildings: by *MM. Chatoney* and *Rivot.* Compt. rend. xlii. 1119; xliii. 373.

Butter.—Determination of butter in milk: by *M. Marchand.* Chem. Gaz. 1856, 253.

Byssus.—On the shells of the mollusca, the byssus, and the chitin question: by *J. Schlossberger.* Ann. Ch. Pharm. xcviii. 99; Chem. Gaz. 1856, 327.

C.

Cadmium.—On some new salts of cadmium, and the iodides of barium and strontium: by *H. Croft.* Chem. Gaz. 1856, 121.

—— On some new compounds of chloride of cadmium: by *Karl v. Hauer.* Wien. Akad. Ber. xvii. 331; Chem. Gaz. 1856, 1; J. pr. Chem. lxvi. 176; lxviii. 385.

—— On the quantitative separation of bismuth from cadmium by means of a solution of bichromate of potash: by *J. Löwe.* J. pr. Chem. lxvii. 469.

—— On cadmium-ethyl: by *J. A. Wanklyn.* Chem. Soc. Qu. J. ix. 193.

—— On some new compounds of cadmium: by *Karl v. Hauer.* Wien. Akad. Ber. xx. 40; Chem. Gaz. 1856, 466.

Caffein.—New method of preparing caffein: by *M. Puccetti.* Arch. Pharm. lxxxiv. 199; Chem. Gaz. 1856, 50.

Calomel.—On the preparation of calomel from corrosive sublimate by means of sulphurous acid: by *F. Sartorius.* Ann. Ch. Pharm. xcvi. 335.

Camphor.—On the Bornean camphor extracted from madder-alcohol: by *M. Jeanjean.* Compt. rend. xliii. 103.

Caoutchouc.—On the *Hancornia speciosa*, artificial gutta percha, and caoutchouc: by *M. Claussen.* J. Pharm. [3] xxix. 130.

—— On the elasticity of vulcanised caoutchouc; by *M. Boileau.* Compt. rend. xlii. 933.

—— Caoutchouc stoppers. J. pr. Chem. lxvii. 170.

—— Vulcanised caoutchouc. Pharm. J. Trans. xvi. 331.

Capillarity.—On capillary phenomena: by *E. Desains.* Compt. rend. xliii. 1077.

Capryl.—On the formation of caprylic aldehyde: by *J. Bouis.* Ann. Ch. Phys. [3] xlviii. 99; Ann. Ch. Pharm. xcvii. 34.

Carbon.—On crystallised carbon and silicium: by *H. Ste-Claire Deville.* Compt. rend. xlii. 49; Chem. Gaz. 1856, 101.

—— On the manufacture of charcoal powder in cylinders, and the preparation of it by over-heated steam: by *Lieut. Kahl.* J. pr. Chem. lxvii. 385.

—— Experiments made with a view to determine the comparative value of peat and peat-charcoal for agricultural purposes: by *E. W. Davy.* Phil. Mag. [4] xi. 172.

—— Chemical composition of mineral charcoal: by *T. H. Rowney.* Ed. N. Phil. J. (N. S.) ii. 141.

—— On the action of nascent hydrogen on sulphide of carbon: by *A. Girard.* Compt. rend. xliii. 396.

—— On the use of sulphide of carbon for industrial purposes: by *E. Deiss.* Compt. rend. xlii. 207; Chem. Gaz. 1856, 136.

Carbonates.—Volumetric determination of alkaline and earthy carbonates by silver: by *C. Mohr.* Ann. Ch. Pharm. xcix. 197.

—— Examination of certain spathic carbonates—pistomesite, pearlspar, tautoclin, and brownspar: by *Dr. Ettling.* Ann. Ch. Pharm. xcix. 202.

Carbonic Oxide.—Researches on the relations between carbonic oxide and formic acid: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 477; Compt. rend. xli. 955; Ann. Ch. Pharm. xcvii. 125; Chem. Gaz. 1856, 9; J. Pharm. [3] xxix. 321.

Carburetted Hydrogen.—Emission of carburetted hydrogen from the soil. Compt. rend. xli. 410; J. pr. Chem. lxvi. 470.

Caroba.—On caroba leaves and some products from Paraguay: by *M. Reveil.* J. Pharm. [3] xxix. 446.

Casein.—Formation of casein by the putrefaction of fibrin: by *Dr. Gunning.* J. pr. Chem. lxvii. 52.

—— Casein-cement: by *R. Wagner.* Polyt. J. cxi. 301; Pharm. J. Trans. xvi. 223; Chem. Gaz. 1856, 392.

Catalytic Force.—Extract from a memoir on bodies which are decomposed under the influence of the so-called catalytic force: by *MM. Thénard, Sen.* and *Jun.* Ann. Ch. Phys. [3] xlvii. 173.

Catechu.—On catechu and its acids; by *C. Neubauer.* Ann. Ch. Pharm. xcvi. 337; Chem. Gaz. 1856, 126; J. pr. Chem. lxvii. 257; J. Pharm. [3] xxx. 216.

Caterpillars.—Crystals in the malpighian vessels of caterpillars: by *J. Schlossberger.* Ann. Ch. Pharm. xcviii. 354.

Cereals.—Researches on the cereals: by *M. Duvivier.* Compt. rend. xlii. 1173.

Charcoal.—See *Carbon.*

Chemical manufactures.—On ameliorations in the hygiene of chemical manufactures: by *M. Kuhlmann.* J. Pharm. [3] xxx. 381.

Chervil.—On the fleshy root of bulbous chervil (*Chærophyllum bulbosum*): by *M. Payen.* Compt. rend. xliii. 769.

Chicory.—New method of examining mixtures of chicory and coffee: by *J. Horsley.* J. Pharm. [3] xxix. 286.

Chinoline.—Researches on chinoline and its homologues: by *C. G. Williams.* Ed. Phil. Trans. xxi. Pt. 3; Chem. Gaz. 1856, 261; abstr. Proc. Roy. Soc. Edinb. iii. 370.

Chitin.—On the chitin question: by *J. Schlossberger.* Ann. Ch. Pharm. xcviii. 99; Chem. Gaz. 1856, 330.

Chlorates.—Volumetric determination of chlorates by silver: by *C. Mohr.* Ann. Ch. Pharm. xcix. 197.

Chlorides.—On the action of metallic chlorides on iodide of lead: by *A. Engelhardt.* J. pr. Chem. lxvii. 293; Chem. Gaz. 1856, 24.

—— On the reduction of some oxides and chlorides by glucose: by *R. Böttger.* J. Pharm. [3] xxix. 479.

—— On chloride of bismuth: by *H. Rose.* J. pr. Chem. lxvi. 251.

—— On some new compounds of chloride of cadmium: by *Karl. v. Hauer.* Wien. Akad. Ber. xvii. 331; Chem. Gaz. 1856, 1; J. pr. Chem. lxvi. 176; lxviii. 385.

Chlorides.—On the behaviour of solution of chloride of mercury with bases: by *H. Rose*. Berl. Akad. Ber. 1855, 579; Chem. Gaz. 1856, 19.

—— Action of chloride of mercury on the iodides of methyl, ethyl, and amyl: by *M. Schlagdenhauffen*. J. Pharm. [3] xxix. 247.

—— On the action of pentachloride of phosphorus on the fixed acids which give rise to the formation of pyro-acids: by *L. Bodart*. Compt. rend. xliii. 391.

—— On the action of chloride of sulphur on formiate of baryta, acetate of soda, and benzoate of soda: by *W. Heintz*. Pogg. Ann. xcviii. 458; Berl. Akad. Ber. 1856, 263; Chem. Gaz. 1856, 327.

—— Double salt of chloride of potassium with biniodate of potash: by *C. Rammelsberg*. Pogg. Ann. xcvii. 92.

—— On the compounds of tetramethylammonium with iodine and chloride of iodine: by *C. Weltzien*. Ann. Ch. Pharm. xcix. 1.

Chloride of Lime.—See *Hypochlorites*.

Chlorine.—Improvements in the manufacture of chlorine (C. T. Dunlop's patent). Chem. Gaz. 1856, 200.

—— New volumetric method of estimating chlorine in compounds: by *C. Mohr*. Ann. Ch. Pharm. xcvii. 335; Ann. Ch. Phys. [3] xlvii. 375; Chem. Gaz. 1856, 174.

—— Quantitative estimation of chlorine in chlorine-water: by *W. Wicke*. Ann. Ch. Pharm. xcix. 99.

—— On the action of light on chlorine-water: by *W. C. Wittwer*. Pogg. Ann. xcvii. 304.

—— On the effect of chlorine in colouring the flame of burning bodies: by *D. Forbes*. Phil. Mag. [4] xi. 65.

—— On the boiling points of analogous bromine and chlorine compounds: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 265.

—— On the solution of chlorine in water: by *H. E. Roscoe*. Ann. Ch. Phys. [3] xlviii. 197.

Chloroform.—On the action of chloroform on other bodies, and especially on ammonia: by *W. Heintz*. Wien. Akad. Ber. 1856, 61; Chem. Gaz. 1856, 245. J. pr. Chem. lxviii. 56; Pogg. Ann. xcviii. 263.

—— Analysis of the blood of a woman who died after inhaling chloroform: by *M. Jackson*. Compt. rend. xlii. 411.

—— On ether as an antidote to chloroform: by *M. Fabre*. Compt. rend. xliii. 193. Report by *M. Cloquet*, ibid, 353.

Chlorophyll.—On the absorptive power of pure and impure chlorophyll for the sun's rays: by *P. Harting*. Pogg. Ann. xcvi. 543.

Chromium.—The mutual action of chromic acid and the volatile oils: by *J. P. Plummer*. Pharm. J. Trans. xvi. 130.

—— On the chromates of bismuth: by *J. Löwe*. J. pr. Chem. lxvii. 288, 463.

—— On the quantitative separation of bismuth, by means of a solution of bichromate of potash: by *J. Löwe*. J. pr. Chem. lxvii. 464, 469.

—— Note on some new reactions of sesquioxide of chromium: by *G. Chancel*. Compt. rend. xliii. 927; Chem. Gaz. 1856, 454.

Chromium.—Action of carbonic acid on sesquioxide of chromium: by *M. Langlois*. Ann. Ch. Phys. [3] xlviii. 502.

Chrysomela.—Contribution to the physiology of *Chrysomela ænea*: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 348.

Cinnamyl.—On the artificial formation of hydride of cinnamyl: by *L. Chiozza*. Ann. Ch. Pharm. xcvii. 350.

Citrates.—A salt which gives off ammonia when treated with hydrochloric acid. Ann. Ch. Pharm. xcvii. 18.

Cleavage.—On slaty cleavage, as exhibited in the Devonian limestones of Devonshire: by *H. C. Sorby*. Phil. Mag. [4] xi. 20.

—— Comparative view of the cleavage of crystals and slate rocks: by *J. Tyndall*. Pharm. J. Trans. xvi. 237.

Coal.—On the coal and lignite of Austria: by *F. Leeland*. Wien. Geol. Jahrb. ii. 609.

—— On the Cuttack coal of Taleheen. Asiat. Soc. J. 1855, 240.

—— On the coal from Rassitz: by *C. D. Hauer*. Wien. Geol. Jahrb. 1855, 139.

—— Purification of coal: *A. Bérard*. Ann. Min. [5]. ix. 147.

—— On some of the products of the distillation of Boghead coal at low temperatures: by *C. G. Williams*. Proc. Roy. Soc. viii. 119.

—— On the nature of the distillation-products of the Torbane-hill mineral: by *A. Geuther*. Ann. Ch. Pharm. xcvii. 277; Chem. Gaz. 1856, 272.

Cobalt.—Contributions to the chemical history of the cobalt compounds: by *P. Schwarzenberg*. Ann. Ch. Pharm. xcvii. 211; Chem. Gaz. 1856, 146.

—— Cobalt-green: by *R. Wagner*. Pharm. J. Trans. xv. 223.

Cocoa.—On the nutritive properties of the mass which remains after the expression of nuts of cocoa, &c.: by *W. Hamilton*. Pharm. J. Trans. xv. 350.

Coffee.—Chemical report on the mode of detecting vegetable substances mixed with coffee for the purpose of adulteration: by *T. Graham*, *J. Stenhouse*, and *D. Campbell*. Chem. Soc. Qu. J. ix. 33.

—— New method of examining mixtures of chicory and coffee: by *J. Horsley*. J. Pharm. [3] xxix. 286.

Colchicine.—On colchicine: by *M. Oberlin*. J. Pharm. [3] xxx. 341.

Colchicum.—On the fecula and alcohol of colchicum: by *M. Comar*. J. Pharm. [3] xxix. 47.

—— Poisoning by colchicum. Reactions of colchicine: by *M. Casper*. J. Pharm. [3] xxvii. 133.

Collodion.—On collodion: by *L. Hofmann*. Arch. Pharm. cxxxviii. 146; Chem. Gaz. 1856, 383.

—— On the methods of preserving the sensitiveness of collodion plates: by *J. Spiller* and *W. Crookes*. Phil. Mag. [4] xi. 334.

Colorimeter.—Improved colorimeter: by *J. W. Slater*. Chem. Gaz. 1856, 89.

—— On the complementary colorimeter: by *A. Müller*. J. pr. Chem. lxvi. 193.

Colour.—On some new colouring matters, derivatives of dinitrobenzol, dinitronaphthaline, &c.: by *A. H. Church* and *W. H. Perkin*. Chem. Soc. Qu. J. ix. 1; abstr. Proc. Roy. Soc. viii. 48; Chem. Gaz. 1856, 139.

—— Theoretical and practical researches on the fixation of colours in dyeing: by *F. Kuhlmann*. Compt. rend. xlii. 673, 711; Chem. Gaz. 1856, 193, 217.

—— On the solubility of the colouring matter of madder in water, between 100° and 150° C.: by *E. Plessy* and *P. Schützenberger*. Compt. rend. xliii. 167; Chem. Gaz. 1856.

—— Simple process for imparting a deep red colour to bone, ivory, &c. by *R. Böttger*. J. pr. Chem. lxviii. 367.

—— Note on a green dye from China: by *D. Hanbury*. Pharm. J. Trans. xvi. 213.

—— On the action of tin on the blue colour of violets: by *M. Argillis*. J. Pharm. [3] xxx. 194.

—— On a colouring matter extracted from the scarlet monarda (*Monarda didyma*, Linn.): by *M. Belhomme*. Compt. rend. xliii. 382.

—— On a new acid extracted from a Mexican plant, and possibly available in dyeing: by *M. Ramon de la Sagra*. Compt. rend. xlii. 873.

—— On the manufacture of Paris blue: by *G. E. Habich*. Polytechn. J. cxxxviii. 295; Chem. Gaz. 1856, 357.

—— Note on the oils used in the preparation of Turkey red: by *M. Pelouze*. Letter of *MM. Henry* on Turkey red. Compt. rend. xlii. 1196.

—— On Rinman's green: by *R. Wagner*. Kunst and Gewerbebl. f. Bayern, 1856, 83; Chem. Gaz. 1856, 392.

—— On the fixation of colours in dyeing: by *M. Kuhlmann*; (3rd part.) Compt. rend. xliii. 900, 950.

—— Lake colours. Pharm. J. Trans. xvi. 331.

Concretions.—Concretions from the Bojanian organ: by *J. Schlossberger*. Ann. Ch. Pharm. xcviii. 354.

—— Examinations of certain concretions found in the stomach of young chickens: by *MM. Girardin* and *Malbranche*. J. Pharm. [3] xxx. 92.

Conjugated compounds.—Remarks on some physical properties of conjugated compounds: by *M. Berthelot*. Ann. Ch. Phys. [3] xlviii. 322.

Contact-action.—On some phenomena relating to contact-action: by *C. F. Schönbein*. J. Pharm. [3] xxix. 365.

Copper.—Contributions to the metallurgy of copper: by *A. Dick*. Phil. Mag. [4] xi. 409.

—— On the metallurgic treatment of the grey copper ore of the Stephanhütte works in Hungary: by *J. Juhos*. Ann. Min. [5] vii. 53.

—— History and description of the ores and foundries of lead, copper, and silver of Lozère. Ann. Min. [5], vii. 1; viii. 351.

—— On the copper ores of Pashak and Mahaldiram. Asiat. Soc. J. 1855, 251.

—— On copper-bismuth: by *E. Tobler*. J. pr. Chem. lxvii. 205.

Copper.—Method of detecting very small quantities of lead and copper: by *J. Löwenthal.* J. pr. Chem. lxvii. 878; Chem. Gaz. 1856, 476.

—— On copper-bismuth-glance from Wittichen: by *R. Schneider.* Pogg. Ann. xcvii. 476.

—— On the compound of cuprous chloride with carbonic oxide: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 488; Ann. Ch. Pharm. xcviii, 392.

—— On the action of the compounds of cuprous oxide with fatty acids on the organism: by *W. Langenbeck* and *G. Staedeler.* Ann. Ch. Pharm. xcvii. 155.

—— On the occurrence of sulphate of copper on stypcicite from Chili: by *E. Tobler.* Ann. Ch. Pharm. xcvi. 383.

—— On the action of heat upon the oxychloride of copper (atacamite): by *F. Field.* Chem. Soc. Qu. J. ix. 140.

—— On the ammoniacal hyposulphate of copper, and on the ammonio-salts of metals in general: by *E. Schweizer.* J. pr. Chem. lxvii. 430.

—— On a double hyposulphite of sodium and copper: by *W. Schutte.* Compt. rend. xlii. 1267; Chem. Gaz. 1856, 351.

—— New method of detecting traces of lead and copper when associated with other bodies: by *J Löwenthal.* J. pr. Chem. lxvii. 378.

—— A copper determination: by *Th. Fleitmann.* Ann. Ch. Pharm. xcviii. 141; Chem. Gaz. 1856, 211.

—— On the double compounds of cyanogen with copper and ammonia: by *L. Hilkenkamp.* Ann. Ch. Pharm. xcvii. 218; Ann. Ch. Phys. [3] xlvii. 181.

Coprolites.—On a coprolitic deposit in Bohemia: by *Prof. Reuss.* Phil. Mag. [4] xi. 486.

Corn.—Analysis of maize, wheat, beans, barley, rice and millet: by *A. Polson.* J. pr. Chem. lxvi. 320.

Cotton.—Testing of woollen tissues for intermixed cotton: by *A. Overbeck.* Chem. Gaz. 1856, 476.

Creatine.—On the possibility of the artificial formation of creatine and creatinine: by *C. Weltzien.* Ann. Ch. Pharm. c. 191.

Cryptogamic plants.—On the absorption of ammonia and nitrates by cryptogamic plants: by *A. B. Bineau.* Ann. Ch. Phys. [3] xlvi. 60.

Crystalline Form.—Crystallographical researches: by *Schabus.* Wien. Akad. Denkschr. xvi. 200.

—— On a new method of investigating the structure and composition of crystals, with special reference to the varieties of rhombohedral quartz: by *M. Leydolt.* Wien. Akad. Denkschr. xv. 59.

—— On a method of resolving synthetically several of the principal questions of crystallography: by *M. Delafosse.* Compt. rend. xliii. 32.

—— On the rhombotypic hemihedry of the tetragonal system: by *C. F. Naumann.* Pogg. Ann. xcvi. 580.

—— On the crystalline forms of certain chemical compounds: by *W. Keferstein.* Pogg. Ann. xcix. 275.

rystalline Form.—Attempt at a general explanation of hemihedry: by *M. Leymerie*. Compt. rend. xliii. 1042.
—— On the crystalline form of certain chemical compounds: by *C. Marignac*. Compt. rend. xlii. 288.
—— On the crystalline form of certain metalloids: by *E. Mitscherlich*. J. pr. Chem. lxvi. 268; J. Pharm. [3] xxix. 314.
—— On the geometrical isomorphism of crystals: by *H. J. Brooke*. Proc. Roy. Soc. viii. 187.
—— Isomorphism between isomeric bodies, the one active and the other inactive, upon polarised light: by *L. Pasteur*. Compt. rend. xlii. 1259.
—— On polymeric isomorphism: by *T. Scherer*. J. pr. Chem. lxviii. 319.
—— On entiomorphism; and the optical properties of crystals of the tesseral system: by *H. Marbach*. Pogg. Ann. xcix. 451.
Crystallization.—On a new fact relating to crystallization: by *M. Bral*. Compt. rend. xliii. 705.
Crystals.—On the arrangement of the molecules in crystals: by *M. L. Frankenheim*. Pogg. Ann. xcvii. 337, 559.
—— On the movement of floating crystals of certain organic acids: by *A. Schafarik*. Wien. Geol. Jahrb. 1855, 263.
—— On the mode of growth of crystals, and on the causes of the variations of their secondary faces: by *L. Pasteur*. Compt. rend. xliii. 795. Observation by *M. de Sénarmont*. Ibid. 799.
Cumarine.—Preparation of cumarine: by *A. Gössmann*. Ann. Ch. Pharm. xcviii. 66; Chem. Gaz. 1856, 210.
Cyanogen.—Preparation of cyanogen-compounds: by *Brunnquell*. Pharm. J. Trans. xvi. 218.
—— Compounds of cyanogen with the metals of the alkaline earths: by *C. Schulz*. J. pr. Chem. lxviii. 257.
—— On the double compounds of cyanogen with copper and ammonia: by *L. Hilkenkamp*. Ann. Ch. Pharm. xcvii. 218: Ann. Ch. Phys. [3] xlvii. 181.
—— On the cyanides of platinum: by *A. Schafarik*. J. pr. Chem. lxvi. 385.
—— On cyanide of ethyl, and a new mode of formation of ethylamine: by *E. Meyer*. J. pr. Chem. lxviii. 279; Chem. Gaz. 1856, 387.
—— Note on a new method of making ferrocyanide of potassium, and a paracyanogen-compound: by *Lyon Playfair*. Chem. Soc. Qu. J. ix. 128.
—— On the action of concentrated sulphuric acid on ferrocyanide of potassium: by *Chr. Gimm* and *G. Ramdohr*. Ann. Ch. Pharm. xcviii. 127; Chem. Gaz. 1856, 201.
—— On sulphocyanide of potassium considered as one of the normal and constant elements of the saliva: by *M. Longet*. Compt. rend. xlii. 480.
—— Preparation of peroxide of lead by means of ferrocyanide of potassium: by *A. Overbeck*. Arch. Pharm. lxxxvi. 5; Phil. Mag. [4] xi. 407.
—— Manufacture of yellow and red prussiate of potash, Prussian blue, cyanide of potassium, &c. Pharm. J. Trans. xv. 421, 511.
—— Presence of cyanogen in carbonate of soda. Pharm. J. Trans. xvi. 223.

Cyanogen.—On some platino-cyanides: by *P. P. Weselsky.* Wien. Akad. Ber. xx. 282; Chem. Gaz. 1856, 443.

—— On the fluorescence of platinocyanide of potassium: by *R. Böttger.* Pogg. Ann. xcvii. 333.

—— Action of chloride of cyanogen on naphthalamine: by *W. H. Perkin.* Chem. Soc. Qu. J. ix. 8; Ann. Ch. Pharm. xcviii. 236.

—— New process for the preparation of ferrocyanide of potassium: by *R. Brunnquell.* Chem. Gaz. 1856, 409.

—— On the formation of crystallized sulphocyanide (rhodanide) of silver: by *A. Gössmann.* Ann. Ch. Pharm. c. 76.

—— Production of ferrocyanides. Pharm. J. Trans. xvi. 331.

Cylinder.—Analysis of a Babylonian cylinder and amulet: by *J. Spiller.* Phil. Mag. [4] xi. 107.

Cymidine.—On the formation and some of the properties of cymidine, the organic base of the cymol group: by *J. Barlow.* Ann. Ch. Pharm. xcviii. 245.

D.

Density.—On the density of certain substances after fusion and rapid cooling: by *Ch. St.-Claire Deville.* Pogg. Ann. xcvi. 618; Phil. Mag. [4] xi. 144.

—— Researches on the specific gravity, expansion by heat, and boiling points of certain liquids: by *H. Kopp.* Ann. Ch. Pharm. xcviii. 360; Ann. Ch. Phys. [3] xlvii. 412.

—— On a new method of determining the densities of solids by means of an ordinary balance: by *A. Raimondi.* Compt. rend. xliii. 437.

Diabetometer.—Description of the diabetometer: by *M. Robiquet.* Compt. rend. xliii. 920.

—— On a diabetometer for estimating sugar in diabetic urine: by *E. Robiquet.* J. Pharm. [3] xxix. 371; xxx. 377.

Diffusion.—On the diffusion of liquids: by *Fr. Beilstein.* Ann. Ch. Pharm. xcix. 165.

Digestion.—On the digestion and absorption of fatty matters without the aid of the pancreatic juice: by *M. Colin.* Compt. rend. xliii. 55.

Dinitrobenzol.—See *Benzol.*

Dinitronaphthaline.—See *Naphthaline.*

Drying.—On the drying of substances for analysis: by *Fr. Rochleder.* J. pr. Chem. lxvi. 208.

Dyeing.—See *Colour.*

E.

Earths.—Improvements in the manufacture of alkalis and alkaline earths (R. A. Tilghman's patent.) Chem. Gaz. 1856, 359.

Eggs.—Analysis of a fossilised egg from the guano islands: by *A. A. Hayes*. Proc. of Boston Soc. Nat. Hist. v. 150.

—— Preservation of yolk of egg. Pharm. J. Trans. xvi. 222.

—— Analysis of the egg-shell of the ostrich: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 350.

Elements.—On crystallized silicium and carbon. General method of obtaining fixed elementary bodies by means of their volatile combinations. Preparation and properties of the fluoride of aluminium: by *H. Ste.-Claire Deville*. Compt. rend. xlii. 49. [Remarks thereupon by *M. de Senarmont*. Ibid 527.] Chem. Gaz. 1856, 101.

—— New method of preparing aluminium and certain simple substances, metallic and non-metallic: by *H. Ste.-Claire Deville*. Compt. rend. xli. 1053.

Electricity.—Experimental researches in electricity: Thirtieth series: by *M. Faraday*. Phil. Trans. 1856, i. 159; abstr. Proc. Roy. Soc. vii. 523.

—— On the development of electricity which is observed when a liquid leaves the spheroïdal state: by *P. L. Rijke*. Pogg. Ann. xcviii. 500.

—— On the development of electricity by friction: by *E. Becquerel*. Compt. rend. xlii. 46; Pogg. Ann. xcviii. 509.

—— On atmospheric electricity and the formation of clouds, &c.: by *H. Scoutetten*. Compt. rend. xliii. 356.

—— Researches on the development of electricity in voltaic piles: by *E. Becquerel*. Ann. Ch. Phys. [3] xlviii. 200.

—— On an electroscope with double condensation: by *J. M. Gaugain*. Ann. Ch. Phys. [3] xlviii. 170.

—— On atmospheric electricity: by *M. Becquerel*. Compt. rend. xlii. 561.

—— On the electric properties of the tourmaline: by *M. Gaugain*. Compt. rend. xlii. 1264; i. and xliii. 916.

—— On quantitative measurement in statical electricity, and on some new phenomena of electrical forces: by *W. Snow Harris*. Proc. Roy. Soc. viii. 166.

—— A sine-electrometer: by *P. Riess*. Pogg. Ann. xcvi. 513.

—— Method of producing Leuchtenberg's figures in great perfection, and of various colours: by *R. Böttger*. J. pr. Chem. lxviii. 369.

—— On the combination of a number of condensers for the purpose of indicating feeble charges of electricity: by *M. Volpicelli*. Compt. rend. xlii. 402.

—— Preliminary notice on the electric conducting power of the alkali-metals: by *A. Matthiessen*. Phil. Mag. [4] xii. 199.

—— On the electro-chemical decomposition of water acting as a conductor in the phenomena of electrostatic induction: by *L. Soret*. Ann. Ch. Phys. [3] xlvii. 119.

—— On the magnetism and electric conductivity of potassium and sodium: by *M. Lamy*. Compt. rend. xliii. 693.

—— On the law of electric discharge: by *P. Riess*. Phil. Mag. [4] xi. 524.

Electricity.—New voltaic battery. Pogg. Ann. xcviii. 306.

—— Experiments on the effects of electric influence in circumstances analogous to those of induction: by *M. Seguin*. Compt. rend. xli. 1149.

—— On a general law of electric discharge: by *W. Snow Harris*. Phil. Mag. [4] xi. 339.

—— On certain phenomena of electric discharge: by *W. Snow Harris*. Phil. Mag. [4] xii. 136.

—— On the electrodynamic properties of metals: by *W. Thomson*. Proc. Roy. Soc. viii. 50; Phil. Mag. [4] xii. 387.

—— Researches on the development of electricity in voltaic batteries. Part I.: electro-motive force: by *M. Becquerel*. Compt. rend. xlii. 1158.

—— Constant voltaic battery: by *V. Doat*. Compt. rend. xlii. 969.

—— On a continuous voltaic battery especially adapted for telegraphic purposes: by *R. Böttger*. Pogg. Ann. xcix. 233; J. pr. Chem. lxviii. 364.

—— Description of a self-sustaining voltaic battery: by *G. Mathiot*. Sill. Am. J. [2] xxi. 43.

—— On a coal-gas carbon and nitric acid battery: by *J. L.* and *L. Wheeler*. Chem. Soc. Qu. J. ix. 198.

—— On the electromotive force which produces secondary currents: by *M. Gaugain*. Compt. rend. xli. 1164.

—— Researches on the electromotive forces in voltaic combinations formed with two metals and two liquids: by *M. Repellin*. Compt. rend. xli. 948.

—— On the electromotive forces of batteries in which amalgamated metals are used: by *M. Gaugain*. Compt. rend. xlii. 430.

—— Determination of the electromotive force of Doat's battery, and some analogous arrangements: by *J. Regnauld*. Compt. rend. xliii. 47.

—— On the quantity of electricity which flows through the transverse section of a galvanic circuit: by *W. Weber* and *R. Kohlrausch*. Pogg. Ann. xcix. 7.

—— On a new form of the galvanometer: by *C. F. Mohr*. Pogg. Ann. xcix. 102.

—— On a method of exhibiting fine galvanometric experiments to a large audience: by *M. du Bois-Raymond*. Phil. Mag. [4] xi. 109.

—— On a powerful form of the induction coil, and some new statical and thermal effects of the induction current: by *J. N. Hearder*. Phil. Mag. [4] xii. 377.

—— On a new arrangement of the induction coil: by *J. N. Hearder*. Phil. Mag. [4] xii. 443.

—— On the electricity of tension in a voltaic couple: by *A. de la Rive*. Ann. Ch. Phys. [3] xlvi. 41.

—— Chemical influence of electricity, light and heat: by *C. F. Schönbein*. Pharm. J. Trans. xv. 513.

—— On the electric actions in electrolysis: by *R. Kohlrausch*. Pogg. Ann. xcvii. 382.

—— Electrolytical experiments: by *A. Geuther*. Ann. Ch. Pharm. xcix. 314.

Electricity.—Electrolytical experiments: by *F. Guthrie*. Ann. Ch. Pharm. xcix. 64.

—— Electrolytical investigations: by *G. Magnus*. Phil. Mag. [4] xii. 157; J. pr. Chem. lxviii. 54.

—— On the movements of the ions in electrolysis: by *W. Hittorf*. Pogg. Ann. xcviii. 1.

—— On the decomposition of water by very weak electric currents, especially by machine-electricity: by *H. Buff*. Ann. Ch. Pharm. xcvi. 257.

—— Experiments relating to the question:—Whether the voltaic current can pass through water without decomposing it? by *M. Despretz*. Compt. rend. xlii. 707. Remarks by *A. de la Rive*. Ibid, 710.

—— On the electrical relations of lead and antimony in various conducting liquids: by *G. Gore*. Pharm. J. Trans. xv. 413.

—— Manufacture of steel by electricity. J. Fr. Inst. [3] xxxi. 248.

—— Electric conductivity of aluminium. Pogg. Ann. xcvii. 643.

—— On the electro-chemical relations of tin and iron: by *G. Gore*. J. Pharm. [3] xxix. 363; Pharm. J. Trans. xv. 357.

—— On the position of sodium in the thermo-electric scale: by *G. Gore*. Pharm. J. Trans. xvi. 321.

—— On a method of producing galvanic copper-deposits on gypsum moulds: by *G. Osann*. J. pr. Chem. lxvi. 253.

—— On the motion of liquids in the closed voltaic circuit, and its relation to electrolysis: by *G. Wiedemann*. Pogg. Ann. xcix. 177.

—— On the theory of Nobili's rings: by *W. Beetz*. Pogg. Ann. xcvii. 22.

—— Some experiments showing the apparent conversion of electricity into mechanical force: by *W. R. Grove*. Phil. Mag. [4] xi. 225.

—— On a law of electrical heat: by *P. Riess*. Phil. Mag. [4] xii. 322.

—— On thermo-electric currents: by *W. Thomson*. Phil. Mag. [4] xi. 433.

—— Thermo-electric phenomena in similar metals: by *R. Franz*. Pogg. Ann. xcvii. 34.

—— On the thermo-electric position of aluminium: by *W. Thomson*. Pogg. Ann. xcix. 334; Pharm. J. Trans. xv. 536.

—— Electrophysiological researches: tenth series, pt. I.: by *C. Matteucci*. Proc. Roy. Soc. viii. 209; Phil. Mag. [4] xi. 461.

—— An experimental inquiry undertaken with the view of ascertaining whether the organic actions *Lacteal Absorption*, and *Nutrition*, in the living animal, are accompanied with manifestation of current force: by *H. F. Baxter*. Phil. Mag. [4] xi. 37.

—— Apparatus for collecting gases evolved by electrolysis. J. pr. Chem. lxvii. 173.

—— On the polar decomposition of water by common and atmospheric electricity: by *H. Andrews*. Pogg. Ann. xcix. 493.

Endosmose.—On the endosmose of gases: by *J. Jamin*. Compt. rend. xliii. 234; Phil. Mag. [4] xi. 325; Pogg. Ann. xcix. 327.

Equisetum.—Analysis of the ash of *Equisetum hiemale*: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 350.

Esculetine.—Fluorescence of esculetine: Pogg. Ann. xcviii. 189.

Essences.—See *Volatile Oils*.

Ethal.—On the nature of crude ethal: by *W. Heintz*. Ann. Ch. Pharm. xcvii. 271; Chem. Gaz. 1856, 222.

Ether.—On ether as an antidote to chloroform: by *M. Fabre*. Compt. rend. xliii. 193. Report by *M. Claquet*. Ibid. 353.

—— On a new mode of formation of common ether and its homologues: by *A. Wurtz*. Ann. Ch. Phys. [3] xlvi. 222.

—— Researches on the formation of ether: by *A. Reynoso*. Ann. Ch. Phys. [3] xlviii. 385.

—— On allyl and the allylic ethers: by *MM. Berthelot* and *De Luca*. Ann. Ch. Phys. [3] xlviii. 286.

Etherification.—Facts relating to the history of etherification: by *A. Reynoso*. Compt. rend. xlii. 686, 1070; Chem. Gaz. 1856, 208; J. Pharm. [3] xxx. 37.

—— On sweet oil of wine and the secondary products of etherification: by *C. Blondeau*. J. Pharm. [3] xxix. 249.

Ethers.—Note on the production of formic ether: by *A. H. Church*. Phil. Mag. [4] xi. 527.

—— Process for preparing hydriodic ether: by *E. Soubeiran*. J. Pharm. [3] xxx. 5.

—— On sweet spirits of nitre: by *D. R. Brown*. Pharm. J. Trans. xv. 400.

Ethyl.—On borate of ethyl: by *H. Rose*. Pogg. Ann. xcviii. 245.

—— On cadmium-ethyl: by *J. A. Wanklyn*. Chem. Soc. Qu. J. ix. 193.

—— On cyanide of ethyl, and a new mode of formation of ethylamine: by *E. Meyer*. J. pr. Chem. lxviii. 279; Chem. Gaz. 1856, 387.

—— Action of chloride of mercury on iodide of ethyl: by *M. Schlagdenhauffen*. J. Pharm. [3] xxix. 247.

—— On the compounds of phosphorus with ethyl: by *F. Berlé*. Ann. Ch. Pharm. xcvii. 334.

—— On the compounds of stibethyl: by *W. Merck*. Ann. Ch. Pharm. xcvii. 329; Chem. Soc. Qu. J. ix. 278.

—— On stibethylium and its compounds: by *R. Löwig*. Ann. Ch. Pharm. xcvii. 329.

—— Production of formiate of ethyl from oxalovinic acid: by *A. H. Church*. Phil. Mag. [4] xi. 527; Ann. Ch. Pharm. c. 256.

Ethylamine.—On some compounds of ethylamine: by *E. Meyer*. J. pr. Chem. lxvii. 147; Chem. Gaz. 1856, 206.

—— On some compounds of ethylamine: by *F. L. Sonnenschein*. J. pr. Chem. lxvii. 147.

Ethylene.—On some compounds of ethylene: by *H. L. Buff*. Proc. Roy. Soc. vii. 188.

—— Preliminary notice on sulphocyanide of ethylene: by *H. L. Buff*. Ann. Ch. Pharm. xcvi. 302; J. Pharm. [3] xxix. 159.

Ethylonaphthylamine.—On ethylonaphthylamine: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 117; Chem. Soc. Qu. J. ix. 264; Chem. Gaz. 1856, 332.

Extracts.—On vegetable extracts: by *T. Southall.* Pharm. J. Trans. xv. 350.

Eye.—On the composition of the eyes of Peruvian mummies: by *M. Payen.* Compt. rend. xliii. 707.

F.

Fats.—Chemical history of the fats: by *W. Heintz.* Pharm. J. Trans. xv. 425.

—— Fats and oils. Pharm. J. Trans. xvi. 332.

—— Researches on the chemical nature and properties of the fatty matters contained in bile: by *M. Gobley.* J. Pharm. xxix. 241.

—— On the nature of the grease in the wool of the sheep: by *M. Chevreul.* Compt. rend. xliii. 130; Chem. Gaz. 1856, 343.

—— On the assimilative properties of various fatty bodies: by *M. Berthé.* Compt. rend. xlii. 890.

—— On the digestion and absorption of fatty substances without the aid of the pancreatic juice: by *M. Colin.* Compt. rend. xliii. 55.

—— On the saponification of fats by anhydrous oxides: by *J. Pelouze.* Compt. rend. xlii. 1081; Ann. Ch. Phys. [3] xlvii. 371; Chem. Gaz. 1856, 283.

Fecula.—On fecula and alcohol from colchicum: by *M. Comar.* J. Pharm. [3] xxix. 47.

Fermentation.—Researches on fermentation: by *M. Berthelot.* Compt. rend. xliii. 236: J. Pharm. [3] xxx. 269.

—— Researches on the fermentation of fatty bodies: by *F. Baudet.* J. Pharm. [3] xxix. 274.

—— On the heat and mechanical power produced by vinous fermentation: by *M. Dubrunfaut.* Compt. rend. xlii. 945.

Fibrin.—On a peculiar modification of fibrin: by *E. v. Gorup-Besanez.* J. Pharm. [3] xxix. 240.

—— Formation of casein by the putrefaction of fibrin: by *Dr. Gunning.* J. pr. Chem. lxvii. 52.

Files.—Analysis and preparation of an alloy for composition-files: by *A. Vogel.* N. Jahrb. Pharm. iv. 138; Chem. Gaz. 1856, 54.

Filtration.—On the rate of filtration of different liquids through animal membranes: by *W. Schmidt.* Pogg. Ann. xcix. 337.

Fire.—On the so-called new Greek fire: by *R. Böttger.* J. pr. Chem. lxviii. 305.

Fire-damp.—On the relations between explosions of fire-damp and cyclones or circular hurricanes: by *T. Dobson.* Compt. rend. xiii. 157.

Flame.—On the effect of chlorine in colouring the flame of burning bodies: by *D. Forbes.* Phil. Mag. [4] xi. 65.

—— On a peculiar behaviour of nitrogenous bodies in the blowpipe-flame: by *A. Vogel, Jun.*, and *C. Reischauer.* J. Pharm. [3] xxx. 79; N. Repert. Pharm. v. 153; Chem. Gaz. 1856, 355.

Flame.—On the chemical actions in the flame of coal-gas: by *H. Landolt.* Pogg. Ann. xcix. 389.

—— Characters of the flame of bisulphide of carbon. Pharm. J. Trans. xv. 563.

—— On the prismatic spectra of the flames of compounds of carbon and hydrogen: by *W. Swan.* Proc. Roy. Soc. Ed. iii. 376.

Flour.—On the examination of flour and bread: by *L. E. Rivot.* Compt. rend. xlii. 635; Ann. Ch. Phys. [3] xcvii. 50.

Fluorescence.—See *Light.*

Fluorine.—Researches on the fluorides: by *E. Fremy.* Ann. Ch. Phys. [3] xlvii. 5.

—— On the compounds of tantalum with fluorine: by *H. Rose.* Pogg. Ann. xcix. 481.

—— Presence of fluorine in the blood: by *J. Nickles.* Compt. rend. xliii. 885.

—— On the metallic fluorides: by *H. Ste.-Claire Deville.* Compt. rend. xlii. 970.

—— On the transformation of the fluoride of aluminium and sodium into aluminate of soda: by *C. Tissier.* Compt. rend. xliii. 102; Chem. Gaz. 1856, 344.

—— Action of phosphate of soda on fluor-spar at a red heat: by *H. Briegleb.* Ann. Ch. Pharm. xcvii. 95; Chem. Gaz. 1856, 149.

Fodder.—See *Nutrition.*

Formiate.—Production of formic ether from oxalovinic acid: by *A. H. Church.* Phil. Mag. J. [4] xi. 527; Ann. Ch. Pharm. c. 256.

Formiates.—Action of chloride of sulphur on formiate of baryta: by *W. Heintz.* Pogg. Ann. xcviii. 458.

Fulminates.—On the composition of fulminating mercury, and on some of the products of its decomposition: by *L. Schischkoff.* Ann. Ch. Pharm. xcvii. 53.

Fulminating Silver.—On the composition of fulminating silver: by *O. B. Kühn.* Chem. Gaz. 1856, 189.

Furfurine.—On furfurine: by *L. Svanberg* and *C. E. Bergstrand.* J. pr. Chem. lxvi. 239; Ann. Ch. Phys. [3] xlvi. 372; Chem. Gaz. 1856, 151.

G

Gall-nuts.—On English gall-nuts: by *M. Vinen.* J. Pharm. [3] xxx. 290.

Galvanometer.—See *Electricity.*

Gas.—Manufacture of gas: by *T. Dimsdale.* J. Fr. Inst. [3] xxxi. 25.

—— On the manufacture of coal-gas: Ann. Min. [5] viii. 1.

—— Illuminating gas from wood. J. Fr. Inst. [3] xxxi. 270.

—— On gas-furnaces: by *C. Sching.* J. Fr. Inst. [3] xxxi. 270; 326.

—— Apparatus for the continuous evolution of gas: by *M. Schlagdenhauffen.* J. Pharm. [3] xxix. 216.

Gas.—Effects of the presence of sulphur in coal gas. Pharm. J. Trans. xvi. 323.

Gases.—Fundamental principles of a theory of gases: by *A. Krönig*. Pogg. Ann. xcix. 315.

—— Relation between the heat-capacity, temperature, and density of gases in so far as they follow Mariotte's law; and application of this relation to the strata of the atmosphere, the barometric measurement of heights, and the determination of the mean height of the atmosphere: by *Captain v. Seydlitz*. Pogg. Ann. xcviii. 77.

—— On the connexion between the doctrine of the equivalency of heat and mechanical work, and the comportment of permanent gases: by *R. Clausius*. Pogg. Ann. xcviii. 173.

—— On the law of absorption for ammoniacal gas: by *L. Carius*. Ann. Ch. Pharm. xcix. 129.

—— On the comparative velocity of the escape of different gases: by *E. Baudrimont*. J. Pharm. [3] xxix. 266.

—— On the endosmose of gases: by *J. Jamin*. Pogg. Ann. xcix. 327; Compt. rend. xliii. 234; Phil. Mag. [4] xi. 325.

—— Experiments on the comparative duration of the flow of gas: by *E. Baudrimont*. Compt. rend. xlii. 398.

—— On the solubility of gases in saline solutions, with reference to the theory of respiration: by *M. Fernet*. Ann. Ch. Phys. [3] xlvii. 360; Compt. rend. xl. 1237.

—— Apparatus for transporting and transferring measured gaseous mixtures: by *H. Hlasiwetz*. Ann. Ch. Pharm. xcvii. 241.

Getah.—On Geta Lahoe: by *Prof. Kaiser*. Kunst-und Gewerbebl. für Bayern. 1856, 109; Chem. Gaz. 1856, 352.

Glandular Secretions.—On the chemical constituents of certain glandular secretions: by *E. v. Gorup-Besanez*. Ann. Ch. Pharm. xcviii. 1.

Glass.—On basaltic glass: by *C. Stickel*. Chem. Gaz. 1856, 180.

—— On the action of water upon glass: by *J. Pelouze*. Compt. rend. xliii. 117; Chem. Gaz. 1856, 341.

—— On the silvering of glass; with some observations on divided gold: by *M. Faraday*. Pharm. J. Trans. xvi. 149.

—— On the silvering and gilding of glass: by *J. Liebig*. Ann. Ch. Pharm. xcviii. 132; Chem. Gaz. 1856, 213.

—— On the manufacture of crown and sheet glass. J. Fr. Inst. [3] xxxii. 205, 275.

Glucose.—See *Sugar*.

Glycerine.—Action of the chlorides and bromides of phosphorus on glycerine: by *MM. Berthelot* and *De Luca*. Compt. rend. xliii. 98; Chem. Gaz. 1856, 348.

—— Note on glycerine: by *M. Dalpiaz*. J. Pharm. [3] xxx. 221.

—— New note on glycerine: by *M. Cap*. J. Pharm. [3] xxix. 209.

—— On the solubility of lime in an aqueous solution of glycerine: by M. *Berthelot*. Ann. Ch. Phys. [3] xlvi. 173.

—— Action of iodide of phosphorus on glycerine; 3rd memoir. Allyl and the allylic ethers: by *MM. Berthelot* and *De Luca*. Ann. Ch. Phys. [3] xlviii. 286.

Glycerine.—Action of the chlorides and bromides of phosphorus upon glycerine: by *MM. Berthelot* and *De Luca*. Ann. Ch. Phys. [3] xlviii. 304.

Glycogeny.—New researches on the glycogenic question: by M. *Chauveau*. Compt. rend. xlii. 1008.

Glycosury.—See *Sugar* and *Urine*.

Glycol.—On glycol, or diatomic alcohol: by *A. Wurtz*. Compt. rend. xliii. 199; Chem. Gaz. 1856, 361; Ann. Ch. Pharm. c. 110.

Glycols.—Researches on acetal and on the glycols: by *A. Wurtz*. Compt. rend. xliii. 478; Ann. Ch. Phys. [3] xlviii. 378; Ann. Ch. Pharm. c. 110.

Gold—On the possible origin of veins of gold in quartz and other rocks: by *L. L. B. Ibbetson*. Phil. Mag. [4] xii. 73.

—— On the gold-dust of Midriapore: Asiat. Soc. J. 1855, 250.

—— On divided gold: by *M. Faraday*. Pharm. J. Trans. xvi. 149.

—— On the silvering and gilding of glass: by *J. Liebig*. Ann. Ch. Pharm. xcviii. 132; Chem. Gaz. 1856, 213.

—— On a new gold varnish, which does not lose its colour by exposure to air and light. Chem. Gaz. 1856, 34.

—— New process for gilding and silvering metals: by *C. Guérin*. Compt. rend. xliii. 808.

Goniometer.—On a new goniometer: by *W. Haidinger*. Pogg. Ann. xcvii. 590.

Graduated Solutions.—On the use of bisulphate of potash in the preparation of graduated solutions: by *E. Hubert*. J. Pharm. [3] xxx. 90.

Grain.—On the preservation of grain: by *M. Doyere*. Compt. rend. xli. 1240.

Graphite.—See *Minerals*.

Guano.—On the guano of the Chincha Islands, and the birds which produce it: by *M. Raymondi*. Compt. rend. xlii. 735.

—— On granat-guano: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 344.

—— Loss of ammonia by Peruvian guano: by *A. Bobierre*. Compt. rend. xliii. 757.

Gum.—On the gums of Senegal: by *L. Soubeiran*. J. Pharm [3] xxx. 53.

Gums.—The gums and resins of commerce: by *P. L. Simmonds*. J. Fr. Inst. [3] xxxii. 177, 279.

Gun Cotton.—New gun cotton. Pharm. J. Trans. xv. 430.

Gutta Percha.—On the *Hancornia speciosa*, artificial gutta percha and caoutchouc: by *M. Claussen*. J. Pharm. [3] xxix. 130.

—— Solution of gutta percha. Pharm. J. Trans. xvi. 142.

—— On the solution of gutta percha. J. Pharm. [3] xxx. 367.

Gypsum.—On the use of burnt gypsum for clarifying turbid wines, preventing them from turning sour, and removing any acetic acid that may be present: by *D. Hessel*. Ann. Ch. Pharm. xcviii. 334.

H

Hæmatosin.—On the preparation of hæmatosin and albumin for technical purposes: by *J. Pillans*. Polyt. J. cxl. 298; Chem. Gaz. 1856, 390.

Hair.—On hair and horny substance: by the *Freiherr von Bibra*. Ann. Ch. Pharm. xcvi. 289; J. pr. Chem. lxvii. 261.

Hancornia.—On the *Hancornia speciosa*, artificial gutta percha and caoutchouc: by *M. Claussen*. J. Pharm. [3] xxix. 130.

Health of Towns.—On the preservation of the health of towns: by *Hervé Mangon*. Ann. Ch. Phys. [3] xlvii. 368.

Heat.—On the heat in the sun's rays: by *E. Foote*. Sill. Am. J. [2] xxii. 377, 382.

—— On the theory of heat: by *A. Harrison*. Phil. Mag. [4] xxii. 397.

—— On the dynamical theory of heat, Part VI.—Thermoelectric currents: by *W. Thomson*. Phil. Mag. [4] xi. 433.

—— On a modified form of the second fundamental theorem in the mechanical theory of heat: by *R. Clausius*. Phil. Mag. [4] xii. 81.

—— On the motion of heat in a given system of points: by *M. Duhamel*. Compt. rend. xliii. 1.

—— On heat as the equivalent of work: by *R. Hoppe*. Pogg. Ann. xcvii. 30; Phil. Mag. [4] xii. 75.

—— On heat as the equivalent of work: by *W. J. Macquorn Rankine*. Phil. Mag. [4] xii. 103.

—— On the connection between the doctrine of the equivalency of heat and mechanical work, and the behaviour of permanent gases: by *R. Clausius*. Pogg. Ann. xcviii. 173.

—— Experimental researches on animal heat: by *Cl. Bernard*. Compt. rend. xliii. 329, 561.

—— On the thermal effects of fluids in motion: by *W. Thomson* and *J. P. Joule*. Proc. Roy. Soc. viii. 41, 178; Pogg. Ann. xcvii. 576.

—— On the heat produced by the influence of a magnet, on moving bodies: by *L. Foucault*. Pogg. Ann. xcvi. 625.

—— On the heat and mechanical power generated by vinous fermentation: by *M. Dubrunfaut*. Compt. rend. xlii. 945.

—— On a circumstance attended with production of heat: by *M. Viard*. Compt. rend. xli. 1171.

—— On the existence of multiple proportions in the quantities of heat, or equivalent alteration in the internal space of bodies, caused by definite changes of state, as produced by chemical combination or otherwise: by *Thomas Woods*. Proc. Roy. Soc. viii. 4; Chem. Gaz. 1856, 116. [Remarks by *J. P. Joule*, ibid. 62.]—Further Proc. Roy. Soc. viii. 211.

—— On the heat of chemical combination: by *T. Woods*. Phil. Mag. [4] xii. 65.

—— Absorption of heat by decomposition: by *T. Woods*. Phil. Mag. [4] xii. 74, 237.

Heat.—On the measurement of the permanent expansion which cast iron suffers when heated, and the methods therein adopted for determining high temperatures: by *A. Hermann* and *P. Herter*. Pogg. Ann. xcvii. 489.

—— On the heat absorbed in chemical decompositions: by *J. P. Joule*. Phil. Mag. [4] xii. 155, 321.

—— On the production of very high temperatures: by *H. Ste. Claire Deville*. Ann. Ch. Phys. [3] xlvi. 182. Pharm. J. Trans. xvi. 215.

—— On the changes of volume which accompany rise of temperature and fusion: by *H. Kopp*. Ann. Ch. Phys. [3] xlvii. 291.

—— On the specific heat of certain elementary bodies, and on the isomeric modifications of selenium: by *V. Regnault*. Pogg. Ann. xcviii. 396; Ann. Ch. Phys. [3] xlvi. 257.

—— Relation between the heat-capacity, temperature and density of gases, in so far as they are subject to Mariotte's law: by *Captain von Seydlitz*. Pogg. Ann. xcviii. 77.

—— On the relation between the temperature and tension of vapour: by *M. Coste*. Compt. rend. xliii. 90.

—— On the calculation of the latent heat of vapours: by *M. Legrand*. Compt. rend. xlii. 213; Pogg. Ann. xcviii. 349.

—— Researches on the specific gravity, expansion by heat, and boiling points of certain liquids: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 367; Ann. Ch. Pharm. [3] xlvii. 412.

—— On the boiling points of analogous bromine and chlorine compounds: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 265.

—— On the boiling points of saturated saline solutions: by *P. Kremers*. Pogg. Ann. xcix. 25.

—— On the curves of solubility of certain salt-atoms, and on the boiling points of saturated solutions: by *P. Kremers*. Pogg. Ann. xcvii. 1.

—— Phenomena attending ebullition. Pogg. Ann. xcviii. 512.

—— On the continued boiling of a supersaturated solution of sulphate of soda, after removal from the source of heat: by *R. Böttger*. J. pr. Chem. lxviii. 366.

—— On the heat-conducting power of metals: by *H. J. Gouilland*. Ann. Ch. Phys. [3] xlviii. 47.

—— On the temperature at which liquids cease to wet the containing vessel: by *C. Wolf*. Pogg. Ann. xcviii. 643.

—— On the congelation of vesicular vapour, and on glacial arrows: by *J. Fournet*. Ann. Ch. Phys. [3] xlvi. 203.

—— On a law of electrical heat: by *P. Riess*. Phil. Mag. [4] xii. 322.

—— Thermo-electric phenomena in similar metals: by *R. Franz*. Pogg. Ann. xcvii. 34.

—— On Negretti and Zambra's maximum thermometer. Pogg. Ann. xcix. 336.

Helianthus.—Alcoholic extract from the stems of *Helianthus tuberosus* (Jerusalem artichoke), by *M. Berard*. J. Pharm. [3] xxix. 463.

Heliographic engraving.—See *Photography*.

Hops.—New method of detecting the presence of sulphur in hops: by *R. Wagner*. Chem. Gaz. 1856, 134.

Horn.—On hair and horny substance: by the *Freiherr v. Bibra*. Ann. Ch. Pharm. xcvi. 289; J. pr. Chem. lxvii. 261.

—— On a mode of giving a metallic surface to horn: by *M. Meunier*. Chem. Gaz. 1856, 374.

Horse-chestnut.—On the constituents of the horse-chestnut: by *Fr. Rochleder*. J. pr. Chem. lxvi. 246.

Horse-flesh.—On the use of horse-flesh as food: by *Is. Geoffrey St. Hilaire*. Compt. rend. xliii. 455.

Horse-radish.—On the distinctive characters of the roots of monks-hood (*Aconitum napellus*), and horse-radish (*Cochlearia armoracia*): by *R. Bentley*. Pharm. J. Trans. xv. 449.

Hydrocarbons.—On the synthesis of hydrocarbons: by *Berthelot*. Compt. rend. xliii. 236; Chem. Gaz. 1856, 367.

—— On the prismatic spectra of the flames of compounds of carbon and hydrogen: by *W. Swan*. Ed. Phil. Trans. xxi. pt. 3, 411; abstr. Proc. Roy. Soc. Ed. iii. 376.

—— On the artificial formation of hydrocarbons: by *M. Berthelot*. Ann. Ch. Pharm. c. 122.

—— On the constitution and chemical nature of the hydrocarbons: by *H. L. Buff*. Ann. Ch. Pharm. c. 219.

Hydrochinone.—On the supposed identity of oxyphenic acid with colourless hydrochinone: by *R. Wagner*. J. pr. Chem. lxvii. 490.

Hydrogen.—On ozone-hydrogen: by *G. Osann*. Pogg. Ann. xcviii. 181.

—— Further experiments showing the difference between electrolytic hydrogen and that which is prepared in the ordinary way: by *G. Osann*. Pogg. Ann. xcvii. 327.

—— Combustion of hydrogen in a limited volume of oxygen. J. pr. Chem. lxvii. 174.

—— On the action of nascent hydrogen on sulphide of carbon: by *A. Girard*. Compt. rend xliii. 396.

—— On the relations of certain bodies differing by H_2 and O_2: by *T. S. Hunt*. Chem. Gaz. 1856, 41; Compt. rend. xli. 1167.

Hypochlorites.—Valuation of chloride of lime by means of sulphate of lime. Pharm. J. Trans. xv. 518.

—— On the behaviour of clear alkaline solutions of chloride of lime when heated: by *G. Schlieper*. Ann. Ch. Pharm. c. 171.

Hyposulphates.—On the ammoniacal hyposulphate of copper, and on the ammonio-salts of metals in general: by *E. Schweizer*. J. pr. Chem. lxvii. 430.

Hyposulphites.—On the use of hyposulphite of soda in quantitative analysis: by *H. Vohl*. Ann. Ch. Pharm. xcvi. 237; J. Pharm. [3] xxix. 74; J. pr. Chem. lxvii. 177; Chem. Gaz. 1856, 175.

—— On a double hyposulphite of sodium and copper: by *W. Schutte*. Compt. rend. xlii. 1267; Chem. Gaz. 1856, 351.

—— On commercial hyposulphites: by *M. Schlagdenhauffen*. J. Pharm. [3] xxx. 81.

Hyraceum.—On hyraceum: by *L. Soubeiran*. J. Pharm. [3] xxix. 379.

I.

Illumination.—On the products of the dry distillation of the Rhenish bituminous schist, of Saxon and Thuringian lignite, and their application as light-giving materials: by *H. Vohl*. Ann. Ch. Pharm. xcviii. 181.

—— See *Light*.

Incandescence.—On the incandescence of metal wires in alcoholic vapour: by *H. Reinsch*. Arch. Pharm. cxxxiv. 187; Chem. Gaz. 1856, 72; Phil. Mag. [4] xi. 246.

Incrustation.—On the prevention of incrustation in steam boilers: by *W. Duntee*. Pharm. J. Trans. xv. 317.

Infusoria.—Examination of the green matter of the true infusoria: by the *Prince of Salm-Horstmar*. Pogg. Ann. xcvii. 331; Phil. Mag. [4] xi. 326.

Ink.—Brown ink for marking linen. Chem. Gaz. 1856, 78.

Inosite.—On the occurrence of inosite, uric acid, &c., in the animal body: by *A. Cloëtta*. Ann. Ch. Pharm. xcix. 289; Ann. Ch. Phys. [3] xlvi. 369; J. pr. Chem. lxvi. 211; Chem. Gaz. 1856, 61.

Insolubility.—On the conditions of the insolubility of bodies: by *Dr. Mohr*. Ann. Ch. Pharm. c. 53.

Inuline.—Note on inuline: by *M. Dubrunfaut*. Compt. rend. xlii. 803.

Iodates.—Volumetric determination of iodates by silver: by *C. Mohr*. Ann. Ch. Pharm, xcix. 197.

Iodides.—Action of chloride of mercury on the iodides of methyl, ethyl, and amyl: by *M. Schlagdenhauffen*: J. Pharm. [3] xxix. 247.

—— On the iodides of barium and strontium: by *H. Croft*. Chem. Gaz. 1856, 125.

—— On the behaviour of iodide of silver with ammonia: by *A. Vogel*. Phil. Mag. [4] xii. 157; Chem. Gaz. 1856, 250.

—— On the action of metallic chlorides upon iodide of lead: by *A. Engelhardt*. Chem. Gaz. 1856, 24.

—— On the action of the oxygen-compounds of nitrogen on iodide of potassium in presence of water: by *M. Béchamp*. Compt. rend. xliii. 388.

—— Test for carbonate and iodate of potash in iodide of potassium: by *W. Copney*. Pharm. J. Trans. xv. 504; J. Pharm. [3] xxx. 119.

—— On iodide of potassium as a test for ozone: by *S. Cloez*. Compt. rend. xliii. 38; Phil. Mag. [4] xi. 237.

—— Action of chloride of mercury on some organic iodides: by *M. Schlagdenhauffen*. J. Pharm. [3] xxx. 38.

Iodine.—On the crystalline form of iodine: by *E. Mitscherlich*. Pogg. Ann. xcviii. 547; Ann. Ch. Phys. [3] xlvi. 308; J. pr. Chem. lxvi. 257.

—— New method of detecting iodine and its compounds in the wet way: by *F. Payen*. J. Pharm. [3] xxix. 127.

Iodine.—On iodide of silver: by *H. Ste.-Claire Deville.* Compt. rend. xliii. 970.

—— Detection of iodine in mineral waters: by *J. Liebig.* Ann. Ch. Pharm. xcviii. 51; Ann. Ch. Phys. [3] xlvii. 193; Chem. Gaz. 1856, 212.

—— On the supposed existence of iodine, and detection of nitric acid, in the air: by *M. Kletzinsky.* Chem. Gaz. 1856, 247.

—— On the double salts of biniodate of potash with chloride of potassium and sulphate of potash: by *C. Rammelsberg.* Pogg. Ann. xcvii. 92.

—— Action of hydriodic acid on silver: by *H. Sainte-Claire Deville.* Compt. rend. xlii. 894.

—— On the use of vapour of iodine as a test for traces of mercury: by *C. Brame.* Compt. rend. xliii. 322.

—— On the behaviour of iodine with sulphite of soda: by *Dr. Braune.* Chem. Gaz. 1856, 348.

—— Use of iodine as an antidote for belladonna. J. Pharm. xxix. 219.

—— On teriodide of bismuth: by *R. Schneider.* Pogg. Ann. xcix. 470.

—— On the behaviour of iodide of mercury with ammonia: by *J. Nessler.* Chem. Gaz. 1856, 446, 463.

——On the compounds of tetramethylammonium with iodine and chloride of iodine: by *C. Weltzien.* Ann. Ch. Pharm. xcix. 1.

—— Note on iodised oil: by *M. Hugonneng.* J. Pharm. [3] xxix. 214.

Iodoform.—On the solution of iodoform in sulphide of carbon: by *E. Humbert.* J. Pharm. [3] xxix. 352.

Iridium.—On the presence of iridium in Californian gold: by *H. Dubois.* Ann. Min. [5] vi. 518.

Iron.—On the occurrence of the ores of iron in the azoic system: by *J. D. Whitney.* Sill. Am. J. [2] xxii. 38.

—— Analysis of the Cleveland iron ore: by *A. Dick.* Phil. Mag. [4] xi. 481; Chem. Gaz. 1856, 226.

—— On the Kunkurs and iron ores of Burdwan. Asiat. Soc. J. 1855, 212.

—— On the iron ores of the Hüttenberg, Carinthia: by *F. Munichdorfer* and *M. F. Lepold.* Geol. Soc. Qu. J. xii. Part II. 2.

—— Pea-ore from the Thurmberg, near Durlach (Baden): by *C. Stamm.* J. pr. Chem. xxvii. 205.

—— On a specimen of native iron from Liberia, Africa: by *A. A. Hayes.* Sill. Am. J. [2] xxi. 153; Pro. Roy. Soc. Edinb. iii. 327.

—— On the magnetism of iron ores: by *C. B. Greiss.* Pogg. Ann. xcviii. 478.

—— New mode of manufacturing iron and steel without fuel: by *H. Bessemer.* Chem. Gaz. 1856, 336; Pharm. J. Trans. xvi. 182.

—— Improvements in the manufacture of cast iron (Price and Nicholson's patent.) Chem. Gaz. 1856, 300.

—— On the compounds of carbon and iron, and their influence on the production of pig-iron: by *A. Gurlt.* Chem. Gaz. 1856, 230, 254.

—— Conversion of cast-iron into steel. Ann. Min. [5] viii. 373.

—— On the composition of some varieties of foreign iron: by *F. A. Abel.* Chem. Soc. Qu. J. ix. 200.

Iron.—On a large amount of iron and manganese in the ash of a water-plant: by *E. v. Gorup-Besanez.* Ann. Ch. Pharm. c. 106.
—— On the permanent expansion of cast iron by heat: by *A. Ermann* and *P. Herter.* Pogg. Ann. xcvii. 489.
—— On the crystalline structure sometimes produced in wrought iron, compared with that of meteoric iron: by *W. Haidinger.* Wien. Akad. Denkschr. xvi. 354.
—— On the electrical relations of tin and iron in various liquids: by *G. Gore.* Pharm. J. Trans. xv. 357.
—— Preparation of ferroso-ferric oxides: by *M. Sepal.* J. Pharm. [3] xxix. 100.
—— On sesquioxide of iron modified by heat: by *L. Péan de St. Gilles.* Ann. Ch. Phys. [3] xlvi. 47.
—— On a peculiar behaviour of oxalic acid with sesquioxide of iron: by *C. F. Schönbein.* J. pr. Chem. lxvi. 275.
—— On the origin and accumulation of proto-carbonate of iron in the coal measures: by *W. B. Rogers.* Sill. Am. J. [2] xxi. 339.
—— On blue ferroso-ferric phosphate: by *C. G. Wittstein.* Pogg. Ann. xcvii. 158.
—— On some ferroso-ferric phosphates: by *G. Jenzsch.* Pogg. Ann. xcviii. 629.
—— Composition of vivianite from Kertsch, and of blue iron ore: by *H. Struve.* J. pr. Chem. lxvii. 302.
—— On a mode of formation of sulphide of iron: by *M. Chevreul.* Compt. rend. xliii. 128.
—— On the chemical composition of some varieties of arsenical pyrites and arsenide of iron: by *G. A. Behncke.* Pogg. Ann. xcviii. 184.
—— Analysis of a mixture of alumina and sesquioxide of iron. J. Pharm. [3] xxix. 59.
—— On the separation of protoxide of nickel from sesquioxide of iron: by *Ph. Schwarzenberg.* Ann. Ch. Pharm. xcvii. 216; Chem. Gaz. 1856, 133.
—— New method of determining iron in the urine, by means of permanganate of potash: by *Dr. Böcker.* Chem. Gaz. 1856, 263.
—— Remarks on the estimation of sulphur in iron: by *E. C. Nicholson* and *D. S. Price.* Phil. Mag. J. [4] xi. 169.
—— Meteoric.—See *Meteorite.*
—— Action of carbonic acid on sesquioxide of iron: by *M. Langlois* Ann. Ch. Phys. [3] xlviii. 502.
—— On Bessemer's process for the manufacture of malleable iron and steel. J. Fr. Inst. [2] xxxii. 267.
—— Production of iron. Pharm. J. Trans. xvi. 327.
—— On an alloy of lead and iron produced in a blast furnace: by *F. L. Sonnenschein.* Chem. Gaz. 1856, 434.

K

Kumis—The kumis and raky of the Tartars. Pharm. J. Trans. xv. 429.

L

Lanthanum.—On iodated subacetate of lanthanum: by *A. Damour*. Compt. rend. xliii. 976.

Laudanum—Observations on the deposit which forms on the liquid laudanum of Sydenham: by *M. Rivot*. J. Pharm. [3] xxx. 202.

Lead—On the extraction of the silver and lead from the argentiferous galena of Pribram, Bohemia: by *M. Kleszczynsky*. Geol. Soc. Qu. J. xii. Part II. 17.

—— History and description of the mines and foundries of lead, silver, and copper of Lozère. Ann. [5] vii. 1; viii. 351.

—— On the sulphuretted lead-ore of Neu-Sinka, in the Tyrol: by *W. Haidinger*. Wien. geol. Jahrb. vi. 1.

—— On the purification of lead by crystallization: by *W. Baker*. Chem. Gaz. 1856, 372.

—— On the electrical relations of lead and antimony in various conducting liquids: by *G. Gore*. Pharm. J. Trans. xv. 413.

—— New method of detecting traces of lead and copper when associated with other bodies: by *J. Löwenthal*. J. pr. Chem. lxvii. 378.

—— Assays and analyses of a series of products from the argentiferous lead-works of Carnoules (Gard): by *M. Lan*. Ann. Min. [5] ix. 333.

—— On native lead and oxide of lead from Mexico. Ann. Ch. Pharm. c. 127.

—— On an alloy of lead and iron produced in a blast-furnace: by *F. L. Sonnenschein*. Chem. Gaz. 1856, 434.

—— Method of detecting very small quantities of lead and copper: by *J. Löwenthal*. J. pr. Chem. lxvii. 878; Chem. Gaz. 1856, 476.

—— On the quantitative determination of lead: by *A. Vogel, Jun*. Chem. Gaz. 1856, 455.

—— On the preparation of peroxide of lead by chlorine: by *A. Geuther*. Ann. Ch. Pharm. xcvi. 382.

—— Preparation of peroxide of lead by means of ferridcyanide of potassium. Phil. Mag. [4] xi. 407.

—— Cleavage of compressed white lead: by *Warren de la Rue*. Phil. Mag. [4] xii. 157.

—— New methods of assaying the sulphides of lead and antimony: by *A. Levol*. Ann. Ch. Phys. [3] xlvi. 472; Chem. Gaz. 1856, 353.

—— On photographic iodide of lead: by *M. Roussieu*. Ann. Ch. Phys. [3] xlvii. 154; J. Pharm. [3] xxxix. 438.

—— On the action of metallic chlorides on iodide of lead: by *A. Engelhardt*. J. pr. Chem. lxvii. 293. Chem. Gaz. 1856, 24.

—— On commercial acetate of lead: by *J. Mackay*. Pharm. J. Trans. xv. 315.

Leather.—On the proximate composition of leather: by *M. Payen*. Compt. rend. xliii. 933.

Ledum.—On the stearoptene of *Ledum palustre*: by *M. Buchner*. J. Pharm. [3] xxix. 318.

Leucin.—Occurrence of leucin in the tissue of the lungs: by *A. Cloetta*. Chem. Gaz. 1856, 61.

Lichens.—Contributions towards the knowledge of the lichens: by *T. Gerding*. Arch. Pharm. cxxxvii. 1; Chem. Gaz. 1856, 388.

Light.—On solar light, with a description of a simple photometer: by *Mungo Ponton*. Proc. Roy. Soc. Edinb. iii. 355.

—— On a new photometer and polarimeter: by *H. Wild*. Pogg. Ann. xcix. 235.

—— On the change of refrangibility of light; second memoir: by *G. Stokes*. Ann. Ch. Phys. [3] xlvi. 380; Pogg. Ann. xcvi. 522.

—— On the determination of indices of refraction: by *F. Bernard*. Pogg. Ann. xcvii. 141, 145.

—— New application of the induction-light. Pogg. Ann. xcviii. 191.

—— On the absorptive power of pure and impure chlorophyll for the sun's rays: by *P. Harting*, Pogg. Ann. xcvi. 543.

—— On the measurement of the chemical action of light: by *H. E. Roscoe*. Chem. Gaz. 1856, 239.

—— On the action of light on chlorine-water: by *W. C. Wittwer*. Pogg. Ann. xcvii. 304.

—— Reducing action of light on sesquichloride of iron: by *G. Osann*. J. pr. Chem. lxvi. 253.

—— Contribution to the study of fluorescence: by *G. Osann*. Pogg. Ann. xcvii. 329; Phil. Mag. [4] xi. 324.

—— On the power of the flames of sulphide of carbon and sulphuretted hydrogen to excite fluorescence: by *C. H. L. v. Babo* and *J. Müller*. Pogg. Ann. xcvii. 508; Chem. Gaz. 1856, 248.

—— On the fluorescence of platinocyanide of potassium, and the application of the light obtained by burning sulphur or phosphorus in oxygen, to the production of photographs: by *R. Böttger*. J. pr. Chem. lxviii. 363. Pogg. Ann. xcvii. 333.

—— On the fluorescence of a substance contained in the bark of *Fraxinus excelsior*: by the *Prince of Salm-Horstmar*. Pogg. Ann. xcvii. 637, 644.

—— Fluorescence of esculetine. Pogg. Ann. xcviii. 189.

—— On the cause of the phosphorescence of *Agaricus olearius*: by *M. Fabre*. Pogg. Ann. xcvii. 335.

Light Polarised.—On some phenomena of circularly polarised light; new apparatus for circular polarisation and new compensator: by *H. Soleil*. Pogg. Ann. xcvii. 152.

—— On the cause of the variation of rotatory power in starch-sugar, and on the probable existence of two varieties of amorphous glucose: by *M. Béchamp*. Compt. rend. xlii. 640, 896.

—— On the variable rotation of the mammellated glucose from the grape: by *M. Dubrunfaut*. Compt. rend. xlii. 739.

Lignin.—On the products of the transformation of starch and lignin under the influence of alkalis, chloride of zinc, and acids: by *M. Béchamp*. Compt. rend. xlii. 1210; Ann. Ch. Phys. [3] xlviii, 458.

Lime.—On the alteration of quick-lime by exposure to the air: by *G. Wittstein*. Ann. Ch. Pharm. xcvii. 224.

—— On the presence of lime in silk, and the inconvenience which it produces in the operation of cleansing: by *M. Guinon*. Compt. rend. xlii. 239.

—— On the solubility of lime in aqueous solutions of cane-sugar, mannite and glycerine: by *M. Berthelot*. Ann. Ch. Phys. [3] xlvi. 173.

—— On the determination of lime for agricultural purposes: by *Dr. Kraut*. Chem. Gaz. 1856, 227.

—— On oxalate of lime: by *E. E. Schmid*. Ann. Ch.Pharm. xcvii. 225.

Liquids.—On the diffusion of liquids: by *Fr. Beilstein*. Ann. Ch. Pharm. xcix. 165.

—— Researches on the specific gravity, expansion by heat, and boiling points of certain liquids: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 360; Ann. Ch. Phys. [3] xlvii. 412.

—— On the temperature at which liquids cease to moisten the containing vessels: by *C. Wolf*. Compt. rend. xlii. 968; Pogg. Ann. xcviii. 543.

—— On the rate of filtration of different liquids through animal membranes: by *W. Schmidt*. Pogg. Ann. xcix. 337.

Lithia.—On some salts of lithia: by *C. Scheibler*. J. pr. Chem. lxvii. 485.

—— Advantageous process for obtaining lithia from lepidolite: by *C. v. Hauer*. J. pr. Chem. lxviii. 310. Chem. Gaz. 1856, 389.

Lithium.—On lithium and its compounds: by *L. Troost*. Compt. rend. xliii. 921; Chem. Gaz. 1856, 462.

—— Re-determination of the atomic weight of lithium: by *J. W. Mallet*. Sill. Am. J. [2] xxii. 349.

—— On phosphate of soda and lithia, and the quantitative estimation of lithia: by *W. Mayer*. Ann. Ch. Pharm. xcviii. 193. Ann. Ch. Phys. [3] xlvii. 288.

Liver.—Influence of the obliteration of the *vena porta* on the secretion of bile, and on the glycogenic function of the liver: by *M. Oré*. Compt. rend. xliii. 463; Remark by *M. Andral*, ibid. 467.

Lophine.—Contribution to the chemical history of lophine: by *E. Atkinson* and *A. Gössmann*. Ann. Ch. Pharm. xcvii. 283; Chem. Soc. Qu. J. ix. 220.

Lungs.—On the occurrence of inosite, uric acid, taurin, and leucin in the tissue of the lungs: by *A. Cloetta*. Chem. Gaz. 1856, 61.

Luteolin.—Preparation, properties, and percentage composition of luteolin: by *F. Moldenhauer*. Ann. Ch. Pharm. c. 180.

M.

Madder.—On some constituents of madder, and of the products obtained from it, especially on the pectine bodies contained in it: by *P. Schützenberger*. Chem. Gaz. 1856, 176.

Madder.—On the solubility of the colouring matter of madder in water between 100° and 150°: by *E. Plessy* and *P. Schützenberger*. Compt. rend. xliii. 167; Chem. Gaz. 1856, 374.

—— On the essential oil contained in essence of madder: by *M. Jeanjean*. Compt. rend. xlii. 857.—[Remarks by *M. Biot*, ibid. 859].—Chem. Gaz. 1856, 241.

Magnetism.—Further researches on the polarity of the diamagnetic force: by *J. Tyndall*. Phil. Mag. [4] xii. 161.

—— On the heat produced by the influence of a magnet in moving bodies: by *L. Foucault*. Pogg. Ann. xcvi. 625.

—— On the magnetism of iron ores: by *C. B. Greiss*. Pogg. Ann. xcviii. 478.

Magnesia.—On magnesite and the economical production of sulphate of magnesia: by *M. Foetterle*. Geol. Soc. Qu. J. xi. Part II. 43.

—— On the substitution of native sulphate of magnesia for sulphuric acid, in the manufacture of sulphate of soda and hydrochloric acid: by *R. de Luna*. Ann. Ch. Phys. [3] xlvii. 176.

—— On crystallised acetate of magnesia: by *C. v. Hauer*. J. pr. Chem. lxvi. 248; Chem. Gaz. 1856, 61.

Malt.—Analysis of the ashes of malt, malt residues, and malt germs: by *H. Scheven*. J. pr. Chem. lxvi. 315.

Manganese.—Analysis of manganese spar from Oberneisen: by *A. Birnbacher*. Ann. Ch. Pharm. xcviii. 144.

—— Conclusions deduced from a research on the oxides and acids of manganese, the manganates and permanganates: by *P. Thénard*. Compt. rend. xlii. 382.

—— Contribution to the knowledge of the salts of sesquioxide of manganese: by *L. Carius*. Ann. Ch. Pharm. xcviii. 53; Chem. Gaz. 1856, 292.

—— Improved methods of recovering oxide of manganese after it has been used in the manufacture of chlorine (W. H. Balmain's patent). Chem. Gaz. 1856, 79.

—— New method of determining iron in the urine by means of permanganate of potash: by *Dr. Böcker*. Chem. Gaz. 1856, 253.

—— On the crystals of acetate of manganese: by *W. Haidinger*. Wien. Akad. Denksch. xvi. 145.

—— Manganate of potash as a decolorising agent: by *A. Gössmann*. Ann. Ch. Pharm. xcix. 373.

—— On a large amount of iron and manganese in the ash of a water-plant: by *E. v. Gorup-Besanez*. Ann. Ch. Pharm. c. 106.

Mannite.—On the preparation of mannite: by *M. Bonsall*. Arch. Pharm. cxxxiv. 70; Chem. Gaz. 1856, 114.

—— On the production of mannite in marine plants: by *M. Phipson*. Compt. rend. xliii. 1056.

—— On the compounds of mannite with acids: by *M. Berthelot*. Compt. rend. xlii. 1111.

—— On the solubility of lime in an aqueous solution of mannite: by *M. Berthelot*. Ann. Ch. Phys. [3] xlvi. 173.

Manure—Experiments on putrefaction, and on the formation of manures: by *Jules Reiset*. Compt. rend. xlii. 53.
—— On the preparation and preservation of manures: by *C. Brame*. Compt. rend. xlii. 1065.
—— Analyses of manure: by *H. Scherer*. J. pr. Chem. lxvi. 317.
—— On the use of the black manure obtained from furze: by *M. de la Malle*. Compt. rend. xliii. 674.
—— On the extraction of manure from sewage-waters: by *H. Mangon*. Compt. rend. xliii. 964.
Marls.—See *Minerals*.
Matches.—On a substitute for Statham's matches: by *R. Böttger*. J. pr. Chem. lxviii. 363; Pogg. Ann. xcviii. 19.
Meat.—On the salted meats of America: by *J. Girardin*. J. Pharm. [3] xxix. 117.
Medium-property.—On the modification of the medium-property [in chemical combination]: by *P. Kremers*. Pogg. Ann. xcix. 58.
Meerschaum.—Artificial meerschaum: by *L. Wagenmann*. J. pr. Chem. lxvii. 502; Chem. Gaz. 1856, 336.
Mercury.—Examination of a new ore of mercury (native corrosive sublimate): by *M. Besnou*. Mem. Soc. Imp. d. Sc. Nat. de Cherbourg, ii. 41, 207.
—— On a quicksilver deposit near Cividale, Lombardy: by *C. v. Hauer*. Geol. Soc. Qu. J. xii. pt. ii. 8.
—— The mercury of new Almaden, California. Pharm. J. Trans. xv. 558.
—— On mines of mercury. J. Pharm. [3] xxx. 299.
—— On the presence of mercury in the argentiferous native copper of Lake Superior: by *M. Hautefeuille*. Compt. rend. xliii. 166; Phil. Mag. [4] xi. 238.
—— Note on the construction of the barometer, and on the ebullition of mercury in vacuo: by *M. Taupenot*. Compt. rend. xlii. 1186.
—— On various tests for mercury: by *C. Brame*. Compt. rend. xliii. 33.
—— On a method of detecting traces of mercury: by *M. Lassaigne*. Compt. rend. xliii. 165.
—— On the use of vapour of iodine as a test for traces of mercury, and on the reagents used in analyses by means of gases: by *C. Brame*. Compt. rend. xliii. 322.
—— On the behaviour of solution of chloride of mercury with bases: by *H. Rose*. Berl. Akad. Ber. 1855, 579; Chem. Gaz. 1856, 19; J. pr. Chem. lxvi. 191.
—— On neutral nitrate of mercury. J. Pharm. [3] xxx. 121; Pharm. J. Trans. xv. 519.
—— On the preparation of calomel from corrosive sublimate: by *F. Sartorius*. Ann. Ch. Pharm. xcvi. 335.
—— On the behaviour of iodide of mercury with ammonia; and on a new test for ammonia: by *J. Nessler*. Chem. Gaz. 1856, 446, 463.
—— On the transformations of subchloride of mercury under the influence of water, alcohol, and heat: by *M. Berthé*. Compt. rend. xliii. 162; Chem. Gaz. 1856, 370.

Mercury.—Action of chloride of mercury on the iodides of methyl, ethyl, and amyl: by *M. Schlagdenhauffen.* J. Pharm. [3] xxix. 247; xxx. 38.

—— On the behaviour of sulphide of mercury with the compounds of the alkali-metals: by *R. Weber.* Wien. Akad. Ber. 1856, 9; Chem. Gaz. 1856, 187; Pogg. Ann. xcvii. 50.

—— On the composition of fulminating mercury, and on some of its products of decomposition: by *L. Schischkoff.* Ann. Ch. Pharm. xcvii. 53.

—— Decomposition of hydrobromic acid by mercury: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 492.

—— On basic mercuric nitrate: by *M. Ditten.* J. Pharm. [3] xxix. 160.

Metalloids.—On the crystalline form of certain metalloids: by *E. Mitscherlich.* J. pr. Chem. lxvi. 268; J. Pharm. [3] xxix. 314.

Metallurgy.—On Patera's application of certain analytical processes to metallurgy: by *C. v. Hauer.* J. pr. Chem. lxvii. 14.

Metals.—On the heat-conducting power of metals: by *H. J. Gouillaud.* Ann. Ch. Phys. [3] xlviii. 47.

—— On the electrodynamic properties of metals: by *W. Thomson.* Proc. Roy. Soc. viii. 50.

—— On the prevention of the oxidation of metals: by *H. Draper.* Pharm. J. Trans. xv. 564.

—— Preliminary notice on the electric conducting power of the alkali-metals: by *A. Matthiessen.* Phil. Mag. [4] xii. 199.

—— On metalliferous veins, and on the arrangement of crystals of quartz and felspar in granitic rocks: by *J. Durocher.* Compt. rend. xliii. 29.

—— On the incandescence of metal wires in alcoholic vapour: by *H. Reinsch.* Phil. Mag. [4] xi. 246.

—— On the ammonium-molecules of the metals: by *C. Weltzien.* Ann. Ch. Pharm. xcvii. 19, and c. 108; also by *C. Claus.* Ibid. xcviii. 317.

—— On the history of organic compounds containing metals: by *E. Frankland.* Ann. Ch. Pharm. xcix. 333.

—— On the theory of metalliferous veins: by *M. Fournet.* Compt. rend. xliii. 842.

—— On the reciprocal precipitations of metals: by *W. Odling.* Chem. Soc. Qu. J. ix. 289.

Meteorite.—Analysis of a meteoric stone from the desert of Atacama: by *F. Field.* Chem. Soc. Qu. J. ix. 143.

—— Examination of the meteoric iron from Xiquipelco, Mexico: by *W. J. Taylor.* Sill. Am. J. [2] xvi. 374.

—— Analysis of meteoric iron from Mexico: by *E. Pugh.* Ann. Ch. Pharm. xcviii. 383.

—— On the fall of meteorites at Bremevorde. Ann. Ch. Pharm. xcix. 244; xcvi. 626: Pogg. Ann. xcviii. 609.

—— Analysis of the meteorites of Mezö-madaras in Transylvania: by *F. Wöhler* and *E. Atkinson.* Phil. Mag. [4] xi. 141.

—— Examination of a meteorite which fell at Oesel, on the 11th of May, 1855: by *A. Goebel.* Ann. Ch. Pharm. xcviii. 387

Meteorites.—On meteorites from Segowlee and Allahabad. Asiat. Soc. J. 1855, 247.

—— Fall of meteorites in East Flanders. Pogg. Ann. xcix. 63.

—— On a new locality of meteoric iron in the Orange River Country, S. Africa, and a supposed new locality of the same in Mexico: by *C. U. Shepard*. Sill. Am. J. [2] xxi. 213.

—— Analysis of the meteoric iron from Sonora. J. pr. Chem. lxvi. 429.

—— New meteoric iron. J. pr. chem. lxv. 431.

—— Analysis of meteoric iron from Mexico: by *E. Pugh*. Ann. Ch. Pharm. xcviii. 383.

—— Analysis of a meteoric iron from Thüringen: by *W. Eberhard*. Ann. Ch. Pharm. xcvi. 286; J. pr. Chem. lxvii. 382.

Methyl.—Action of chloride of mercury on iodide of methyl: by *M. Schlagdenhauffen*. J. Pharm. [3] xxix. 247.

—— On the action of water upon certain sulphomethylates: by *A. H. Church*. Phil. Mag. [4] xi. 68.

—— On selenmethyl: by *F. Wöhler* and *J. Dean*. Ann. Ch. Pharm. xcvii. 5; Sill. Am. J. [4] xxi. 247.

—— Tremethylamine in human urine: by *V. Dessaignes*. Compt. rend. xliii. 670.

—— On the compounds of tetramethyl-ammonium with iodine and chloride of iodine: by *C. Weltzien*. Ann. Ch. Pharm. xcix. 1.

Methyluramine.—New researches on methyluramine and its derivatives: by *V. Dessaignes*. Ann. Ch. Pharm. xcvii. 339; Chem. Soc. Qu. J. ix. 286; Compt. rend. xli. 1258.

Methylated Spirit.—The use of methylated spirit: by *H. Wilkinson*. Pharm. J. Trans. xv. 351.

—— On methylated spirit and some of its preparations. Pharm. J. Trans. xv. 310.

Milk.—On the normal alteration in the composition of cow's milk at different times of the day: by *Prof. Bödeker*. Ann. Ch. Pharm. xcvii. 150; J. pr. Chem. lxviii. 24.

—— On some variations in the composition, and nutritive power, of cow's milk during the first milk period: by *F. Crusens*. J. pr. Chem. lxviii. 1.

—— Composition and analysis of milk. Pharm. J. Trans. xvi. 135.

—— On the quantities of water and fat in goat's milk at various times of the day: by *W. Wicke*. Ann. Ch. Pharm. xcviii. 124.

—— On the composition of sow's milk: by *H. Scheven*. J. pr. Chem. lxviii.

—— Determination of butter in milk: by *M. Marchand*. Chem. Gaz. 1856, 253.

—— Analytical examination of the lactiform liquid discovered by *MM. Gaudin* and *Choumarra*. J. Pharm. [3] xxx. 271.

—— Volumetric estimation of milk-sugar by means of Soleil's saccharimeter; and determination of the richness of milk: by *M. Poggiale*. J. Pharm. [3] xxx. 321.

Minerals.—Chemical mineralogical contributions: by *E. E. Schmid*. Pogg. Ann. xcvii. 108.

—— Mineralogical notices: by *A. Kenngott*. Wien. Akad. Denkschr. xii. 243; xv. 234; xvi. 142.

Minerals.—Mineralogical notice of the circle of Laghouat: by *M. Ville.* Compt. rend. xlii. 396.

—— Mineralogical notes—Meteorite, Nickel, &c.: by *T. S. Hunt.* Sill. Am. J. [2] xix. 416, 428.

—— Supplements to Dana's Mineralogy. No. 1. Sill. Am. J. [2] xix. 353; No. II. ibid. xxi. 193. No. 111. Ibid. xxii. 246.

—— Five new mineral species—Xanthitane, pyromelane, pyroclusite, glaubapatite, epiglaubite: by *C. U. Shepard.* Sill. Am. J. [2] xxii. 96.

—— New Swedish minerals: by *Igelström* and *Svanberg.* Ofversigt af. Kongl. Vetenskaps-Akad. Förhandl. 1855, 156.

—— Swedish minerals—Orthite, pistazite, prehnitoïd, labrador: by *C. W. Blomstrand.* J. pr. Chem. lxvi. 156.

—— Mineral veins, and East Tennessee copper-mines: by *J. D. Whitney.* Sill. Am. J. [2] xx. 53.

—— On the treatment of rich argentiferous minerals at Joachimsthal, in Bohemia: by *A. Patera.* Chem. Gaz. 1856, 274.

—— On some minerals found at Cherbourg: by *J. Lesdos.* Mem. Soc. Imp. d. Sc. nat. de Cherbourg, ii. 379.

—— On certain minerals in the granites of the coast to the east of Cherbourg: by *J. Lesdos.* Mem. Soc. Imp. d. Sc. nat. de Cherbourg, ii. 98.

—— Chemical composition of some Norwegian minerals: by *D. Forbes.* Ed. N. Phil. J. iii. 1.

—— Analysis of Norwegian minerals—Orthite, euxite, yttrotitanite: by *D. Forbes* and *T. Dahll.* J. pr. Chem. lxvi. 442.

—— Mineralogical observations from Mähren: by *E. F. Glocker.* Wien. geol. Jahrb. stalt, 1855, 95.

—— The mineral species and pseudomorphoses of Pribram, arranged according to their occurrence: by *E. Klecszynski.* Wien. Geol. Jahrb. vi. 46.

—— The minerals of Scarborough: by *Dr. Murray.* Scarb. Phil. Soc. 23rd Rep. 1855, 25.

—— Description of a new mineral from Felsöbanya, in Hungary: by *A. Kenngott.* Pogg. Ann. xcviii. 165.

—— Researches on the artificial formation of minerals, and on the geological conclusions thence resulting: by *M. Durocher.* Compt. rend. xlii. 850.

Minerals: Adularia.—On adularia from the Binnenthal: by *Ch. Heusser.* Pogg. Ann. xcvii. 128.

Allophane.—Analysis of allophane: by *C. T. Jackson,* Proc. of Boston. Soc. of Nat. Hist. v. 120.

Amphibole.—Comparison of augite and amphibole according to their chief crystallographical and optical properties: by *W. Haidinger.* Wien. Akad. Ber. xvii. 456.

Amphibolite.—On the amphibolite of the eastern part of the mountains of Beaujolais: by *M. Drouat.* Ann. Min. [5] viii. 307.

Amygdalophyr.—On amygdalophyr, a felsite mineral associated with weissigite: by *G. Jensch.* Leonhard and Bronn's N. Jahrb. f. Mineral. &c., 1855, 798.

Minerals: Analcime.—Analysis of the so-called leucite (analcime) from the Kaiserstuhl, in the Breisgau: by *C. Stamm.* Ann. Ch. Pharm. xcix. 287; Remark by *Dr. Sandberger*, ibid. 288.

Andalusite.—Andalusite from Katharinenberg, near Wunsiedel, from Robschutz, near Meissen, and from Bräunsdorf, near Freiberg: by *E. E. Schmid.* Pogg. Ann. xcvii. 113.

Arragonite.—On earth-foam or aphrite (Schaumkalk) as a pseudomorph of arragonite: by *G. Rose.* Pogg. Ann. xcvii. 161; J. pr. Chem. lxvii. 309.

Atacamite.—On the action of heat upon the oxychloride of copper (atacamite): by *F. Field.* Chem. Soc. Qu. J. ix. 140.

Basalt.—Experiment on basalt: by *A. Bensch.* Geol. Soc. Qu. J. xii. Pt. II. 19.

— On basalt in Silesia: by *E. Urban.* Wien. K. K. Geol. Reichsanstalt, 1855, 312.

Binnite.—On binnite from the Binnenthal: by *Ch. Heusser.* Pogg. Ann. xcvii. 120.

Bleiniere.—On a substance named *Bleiniere* in modern treatises on mineralogy: by *N. J. Brooke.* Phil. Mag. [4] xii. 136.

Boracite.—On the dense boracite of Stassfurt: by *G. Rose.* Pogg. Ann. xcviii. 632; J. pr. Chem. lxviii. 110.

Boronatrocalcite.—On boronatrocalcite from South America: by *C. Rammelsberg.* Pogg. Ann. xcvii. 301; Phil. Mag. [4] xi. 486.

Brownspar.—Examination of brownspar: by *Dr. Ettling.* Ann. Ch. Pharm. xcix. 204.

Calcite.—On some peculiar specimens of calcite: by *A. Kenngott.* Pogg. Ann. xcvii. 310.

Carnallite.—On carnallite: by *H. Rose.* Pogg. Ann. xcviii. 161.

Cœlestine.—On cœlestine from the neighbourhood of Frohburg. Verhandl. d. naturf. Gesellsch. in Basel. 1855, 295.

Copper Bismuth-glance.—On copper bismuth-glance from Wittichen: by *R. Schneider.* Pogg. Ann. xcvii. 476.

Cryolite.—Occurrence of cryolite: Pogg. Ann. xcviii. 5111.

— On the cryolite of Greenland: by *J. W. Tayler.* Phil. Mag. [4] xii. 551; Geol. Soc. Qu. J. xii. Pt. I. 140.

Datolite.—Further contributions to the crystallographical history of datolite: by *F. H. Schrœder.* Pogg. Ann. xcviii. 34.

Davidsonite.—Note on the "Davidsonite" of Thomson: by *Dr. Heddle.* Phil. Mag. [4] xii. 386.

Diallage.—Analysis of diallage. J. pr. Chem. lxvi. 448.

Diamond.—On the black diamond: by *M. Deseloizeaux.* Ann. Min. [5] viii. 304.

Domite.—On the composition of domite from Puy-de-Dôme: by *G. Lewinstein.* Pogg. Ann. xcviii. 163.

Dopplesite.—On dopplesite: by *G. A. Kenngott.* Wien. Geol. Jahrb. iii. 303.

Dufrenoysite.—On the dufrenoysite, binnite, and adularia, of the Binnenthal: by *Ch. Heusser.* Pogg. Ann. xcvii. 115.

Earth-foam.—On earth-foam, or aphrite, as a pseudomorph of arragonite: by *G. Rose.* J. pr. Chem. lxvii. 308: Pogg. Ann. xcvii. 161.

Minerals: Euclase.—On the composition of euclase: by *A. Damour.* Ann. Min. [5] viii. 79.

Felspar.—On the arrangement of the crystals of quartz and felspar in granitic rocks: by *J. Durocher.* Compt. rend. xliii. 29.

— On the composition of glassy felspar: by *G. Lewinstein.* J. pr. Chem. lxviii. 98.

Fluor-spar.—On remarkable crystals of quartz and fluor-spar: by *A. Kenngott.* Min. Notizen. xiv. 20, 22; Geol. Soc. Qu. J. xii. Pt. II. 20.

— Action of phosphate of soda on fluor-spar at a red heat: by *H. Briegleb.* Ann. Ch. Pharm. xcvii. 95.

Galactite.—On the galactite of Haidinger: by *Dr. Heddle.* Phil. Mag. [4] xi. 272.

Gneiss.—On the red and grey gneiss of the Hartz: by *G. Quincke.* Ann. Ch. Pharm. xcix. 232.

Granite.—On the granites of the S. E. of Ireland: by *S. Haughton.* Geol. Soc. Qu. J. xii. Pt. I. 171.

— On the gneiss and granite of central Bohemia: by *M. Jokely.* Geol. Soc. Qu. J. xii. Pt. II. 5.

Graphite.—Observations on graphite: by *B. C. Brodie.* Ann. Ch. Pharm. xcvii. 128.

— On the graphite of Kumaon and Travancore. Asiat. Soc. J. 1855, 203.

— Crystalline form of pure native graphite: by *J. Löwe.* J. pr. Chem. lxvi. 186.

Gymnite.—On the gymnite of Fleims: by *W. Haidinger.* Wien. Geol. Jahrb. iii. 607.

Hornblende.—Analysis of hornblendes. J. pr. Chem. lxvi. 450.

Hypersthene.—Analysis of hypersthene. J. pr. Chem. lxvi. 447.

Johnstonite.—On johnstonite, from Transylvania. Geol. Soc. Qu. J. xii. Part II. 10.

Jaulingite.—On jaulingite, a new fossil resin from the Jauling, near St. Vert, Lower Austria: by *V. R. v. Zepharovich.* Wien. Akad. Ber. xvi. Part II. 366.

Junkerite.—On junkerite: by *A. Kenngott.* Min. Notizen, xiv. 13; Geol. Soc. Qu. J. xii. Part II. 20.

Labrador.—Analysis of Labrador. J. pr. Chem. lxvi. 447.

Laumontite.—Analysis of laumontite, from the Sarnthal, near Botzen, in the Tyrol: by *H. Gericke.* Ann. Ch. Pharm. xcix. 110.

Lepidolite.—Advantageous process for obtaining lithia from lepidolite: by *C. v. Hauer.* J. Pr. Chem. lxviii. 310; Chem. Gaz. 1856, 389.

Leuchtenbergite.—On leuchtenbergite and its accompanying minerals: hydrargyllite, garnet, perowskite, magnetite, talcapatite, &c., (conclusion): by *G. H. O. Volger.* Pogg. Ann. xcvi. 559.

Leucite.—On the composition and pseudomorphoses of leucite: by *C. Rammelsberg.* J. pr. Chem. lxviii. 238.

— On the chemical composition of leucite and its products of decomposition: by *C. Rammelsberg.* Pogg. Ann. xcviii. 142.

Minerals: Leucophane.—On the identity of composition of leucophane and melinophane, and on some new compounds from the salt bed of Stassfurth: by *C. Rammelsberg*. J. pr. Chem. lxviii. 245. Pogg. Ann. xcviii. 257.

Lievrite.—Analysis of lievrite from Herbornseelbach, in Nassau: by *E. Tobler*. Ann. Ch. Pharm. xcix. 122.

— On the lignites of the Hansbruck, Upper Austria: by *Baron Hungerau*. Geol. Soc. Qu. J. xii. Part II. 16.

Lignite.—On the lignite of Kainach, Styria: by *Dr. Rolle*. Geol. Soc. Qu. J. xii. Part II. 7.

— On the products of the dry distillation of Rhenish bituminous schist, and of Saxon and Thuringian lignite, together with their application as light-giving materials: by *H. Vohl*. Ann. Ch. Pharm. xcvii. 9; xcviii. 181.

— On the products of the dry distillation of several varieties of peat and lignite: by *F. L. Sonnenschein*. J. pr. Chem. lxvii. 142.

— Analysis of the lignite of Cludinier, in Carnia: by *F. Filipuzzi*. Wien. Akad. Ber. xvii. 440; J. pr. Chem. lxviii. 124.

Limestone.—Analysis of twenty-four limestones from South Tyrol: by *A. v. Hubert*. Wien. Geol. Jahrb. iii. 729.

— Simple method of detecting the presence of iron, magnesia, and manganese in dolomites, marls and limestones: by *M. Delanoue*. Bull. Soc. Geol. de France, 1855, 361.—Remarks thereupon by *M. Lassaigne*, ibid. 399.

— On slaty cleavage, as exhibited in the Devonian limestones of Devonshire: by *H. Sorby*. Phil. Mag. [4] xi. 20.

Magnesite.—On a new locality of magnesite in Styria; by *M. Fœtterle*. Wien. Geol. Jahrb. vi. 68.

— On magnesite and the economical production of sulphate of magnesia: by *M. Fœtterle*. Geol. Soc. Qu. J. xi. Part II. 43.

Manganese Spar.—Analysis of manganese spar from Oberneisen: by *A. Birnbacher*. Ann. Ch. Pharm. xcviii. 144.

Marl.—Analysis of two marls from the Lüneburg: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 346.

Melinophane.—See Leucophane.

Mica.—On the pseudomorphous mica of Lomnitz: by *G. v. Rath*. Pogg. Ann. xcviii. 280.

Natrolyte.—Analysis of Scotch natrolites: by *Dr. Heddle*. Phil. Mag. [4] xi. 272.

Opal.—On hydrate of silica, and the formation of opal and quartz: by *O. Maschke*. J. pr. Chem. lxviii. 233.

Pearlspar.—Examination of pearlspar: by *Dr. Ettling*. Ann. Ch. Pharm. xcix. 204.

Parastilbite.—On parastilbite, a new mineral species: by *W. S. v. Waltershausen*. Pogg. Ann. xcix. 170.

Pennine.—On the crystalline form of pennine: by *Ch. Heusser*. Pogg. Ann. xcix. 174.

Peridote.—Note on a titaniferous peridote from Pfunders, in the Tyrol: by *M. Damour*. Compt. rend. xli. 1151; Ann. Min. [5] viii. 90.

Phonolite.—Analysis of phonolite from the Netzomitz mountain in Bohemia: by *J. Jenzsch*. Pogg. Ann. xcix. 417.

Minerals: Pianzite.—On pianzite from Styria: by *A. Kenngott.* Geol. Soc. Qu. J. xii. Part II. 14.

Pistomesite.—Examination of pistomesite: by *Dr. Ettling.* Ann. Ch. Pharm. xcix. 202.

Pozzolano.—On a bed of pozzolano recently discovered in the Haute-Loire: by *M. Bertrand.* Compt. rend. xlii. 550.

Pyrites—On crystals of pyrites in quartz: by *A. Kenngott.* Pogg. Ann. xcviii. 168.

— Analysis of arsenical pyrites and white iron pyrites (Wasserkies): by *H. Vogel,* Leonhard and Bronn's N. Jahrb. f. Mineral. &c. 1855, 674.

Pyrites, Arsenical.—On the chemical composition of some modifications of arsenical pyrites and arsenical iron: by *G. A. Behncke.* Pogg. Ann. xcviii. 184.

Quartz.—Formation of quartz: by *O. Maschke.* J. pr. Chem. lxviii. 233.

— Formation of quartz in the wet-way. J. pr. Chem. lxvii. 191.

— On an irregular crystallisation of quartz: by *A. Kenngott.* Pogg. Ann. xcvii. 628.

— On remarkable crystals of quartz and fluor-spar: by *A. Kenngott.* Min. Notizen, xiv. 20, 22; Geol. Soc. Qu. J. xii. Part II. 20.

— On some faces of quartz: by *Websky.* Pogg. Ann. xcix. 296.

— On the arrangement of crystals of quartz and felspar in granitic rocks: by *J. Durocher.* Compt. rend. xliii. 29.

Rhodonite.—On the crystalline form of rhodonite: by *R. P. Greg.* Phil. Mag. [4] xi. 196.

Rock-crystal.—New mode of determining whether the faces of a plate of rock-crystal which are parallel to each other, are also parallel to the crystallographic axis or inclined to it: by *H. Soleil.* Pogg. Ann. xcvii. 155.

Sandstone.—Analysis of Craighleith sandstone: by *T. Bloxam,* with a preliminary note by *Prof. Wilson.* Proc. Roy. Soc. Edinb. iii. 390.

Saussurite.—Analysis of Saussurite. J. pr. Chem. lxvi. 450.

Schist.—On the products of the dry distillation of Rhenish bituminous schist: by *H. Vohl.* Ann. Ch. Pharm. xcviii. 181.

Serpentine.—On serpentine rock: by *A. A. Hayes.* Sill. Am. J. [2] xxi. 382.

— On serpentines and soapstones: by *S. Haughton.* Phil. Mag. [4] x. 253; J. pr. Chem. lxvii. 383.

Siderite.—On some crystalline forms of siderite: by *A. Kenngott.* Pogg. Ann. xcvii. 99.

Soapstone.—See Serpentine.

Steatite.—On the so-called steatite: by *C. Rammelsberg.* Pogg. Ann. xcvii. 300; Phil. Mag. [4] xi. 407.

Stilpnomelane.—New observations on the occurrence of stilpnomelane: by *E. F. Glocker.* Wien. Akad. Ber. xvii. 401.

Strontianite.—On strontianite, from Radoboj in Hungary: by *W. Haidinger.* Wien. geol. Jahrb. iii. 606.

Tachhydrite.—On tachhydrite, a new mineral from the rock salt of Stassfurth: by *C. Rammelsberg.* Pogg. Ann. xcviii. 261.

Minerals: Tantalite.—Zirconiferous tantalite from Limoges: by *C. Jenzsch.* Pogg. Ann. xcvii. 104.

Tautoclin.—Examination of tautoclin: by *Dr. Ettling.* Ann. Ch. Pharm. xcix. 204.

Tennantite.—On tennantite, a new mineral: by *W. J. Taylor.* Sill. Am. J. 20, 412; J. pr. Chem. lxvii. 192.

Tertiary strata.—On the tertiary strata of the Caucasus and the adjoining countries. On rock-salt and its origin in tertiary strata: by *M. Abich.* Compt. rend. xliii. 227.

Torbanehill mineral.—On the nature and distillation products of the Torbane-hill mineral: by *A. Geuther.* Ann. Ch. Pharm. xcvii. 277.

Tourmaline.—On the electric properties of the tourmaline: by *M. Gaugain.* Compt. rend. xlii. 1264.

Tyrite.—On the mineral called tyrite: by *A. Kenngott.* Pogg. Ann. xcvii. 622.

Vanadiate of Lead.—On the crystalline form and chemical composition of native vanadiate of lead: by *C. Rammelsberg.* J. pr. Chem. lxviii. 244; Pogg. Ann. xcviii. 249.

Vanadinite.—On the composition of vanadinite: by *A. Kenngott.* Pogg. Ann. xcix. 95.

Vesuvian.—On the quantity of water in vesuvian: by *G. Magnus.* J. pr. Chem. lxviii. 310.

Vivianite.—Occurrence of vivianite in human bones in a cemetery: by *J. Nicklès.* Compt. rend. xli. 1069; Chem. Gaz. 1856, 246; J. Pharm. [3] xxix. 94; Sill. Am. J. [2] xxi.

— On the composition of vivianite from Kertsch, and of blue iron ore: by *H. Struve.* J. pr. Chem. lxvii. 302.

Voigtite.—On voigtite, a new mineral from Ehrenberg, near Ilmenau: by *E. E. Schmid.* Pogg. Ann. xcvii. 108.

Völknerite.—On the völknerite of Snarum: by *C. Rammelsberg.* Pogg. Ann. xcvii. 296; Phil. Mag. [4] xi. 407.

Zeolites.—Note on a zeolite mineral from the Isle of Skye: by *J. W. Mallet.* Phil. Mag. [4] xii. 406; Sill. Am. J. [2] xxii. 179.

Zircons.—On the presence of zircons in the tertiary sands of Soret: by *M. de. Serres.* Compt. rend. xlii. 434.

Molluscs.—On the nature of the liquid with which molluscs repair their shells: by *M. de Serres.* Compt. rend. xlii. 822.

Molybdenum.—On molybdate of ammonia as a test for phosphoric and arsenic acid: by *M. Béchamp.* J. Pharm. [3] xxix. 15; Chem. Trans. xv. 429.

—— On the compounds of phosphomolybdic acid with certain bases: by *Max Seligsohn.* J. pr. Chem. lxvii. 470.

Monarda.—On a colouring matter extracted from the *Monarda didyma.* (Linn.) by *M. Belhomme.* Compt. rend. xlii. 382.

Mortar.—On hydraulic mortars: by *A. Winkler.* J. pr. Chem. lxvii. 444.

Muscles.—Researches on the composition of the muscles in the different grades of the animal series: by *Valenciennes* and *Fremy.* J. Pharm. [3] xxviii. 401; Chem. Gaz. 1856, 131; Sill. Am. J. [2] xxii. 9.

Muscular contraction.—Researches on the physical and chemical phenomena of muscular contraction: by *Ch. Matteucci*. Ann. Ch. Phys. xlvii. 129; Compt. rend. xlii. 648.

Mushroom.—Chemical examination of the edible mushroom, with observations on its nutritive value: by *J. Lefort*. J. Pharm. [3] xxix. 190; Compt. rend. xlii. 90.

—— On ozone and ozonic actions in mushrooms: by *C. F. Schonbein*. Phil. Mag. [4] xi. 137; J. pr. Chem. lxvii. 497.

N.

Naphtha.—On Burmese naphtha, or Rangoon tar: by *Warren de la Rue* and *Hugo Müller*. Proc. Roy. Soc. viii. 221.

Naphthalamine.—On the metamorphoses of naphthalamine: by *A. W. Hofmann*. Proc. Roy. Soc. viii. 10; Chem. Gaz. 1856, 119: Phil. Mag. [4] xii. 226.

—— Action of chloride of cyanogen on naphthalamine: by *W. H. Perkin*. Chem. Soc. Qu. J. ix. 8; Ann. Ch. Pharm. xcviii. 236.

Naphthaline.—On some new colouring matters, derivatives of dinitrobenzole and dinitronaphthaline: by *A. H. Church* and *W. H. Perkin*. Chem. Soc. Qu. J. ix. 1.

Naphthalin.—On some derivates of naphthalin: by *L. Dusart*. Ann. Ch. Pharm. xcvii. 138.

Naphthyl.—On ethylonaphthylamine: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 117; Chem. Soc. Qu. J. ix. 264; Chem. Gaz. 1856, 332.

Naphthylamine.—On the action of nitrous acid upon naphthylamine: by *L. Chiozza*. Ann. Ch. Pharm. xcix. 240.

Narcotine.—Test for narcotine. Pharm. J. Trans. xvi. 312.

Nickel.—On the separation of protoxide of nickel from sesquioxide of iron: by *Ph. Schwarzenberg*. Ann. Ch. Pharm. xcvii. 216; Chem. Gaz. 1856, 133.

—— On sulphate of nickel: by *C. Marignac*. Ann. Ch. Pharm. xcvii. 294; Chem. Gaz. 1856, 250.

Niobium.—Researches on niobium: by *R. Hermann*. J. pr. Chem. lxviii. 65.

Nitrates.—What is the function of nitrates in the economy of plants? On some new methods of estimating nitrogen in nitrates in presence of organic matters: by *G. Ville*. Ann. Ch. Phys. [3] xlvi. 314; Compt. rend. xliii. 85, 612.

—— Report on a memoir by *M. G. Ville*, on the function of nitrates in the economy of plants: by *M. Pelouze*. Compt. rend. xlii. 679.

—— On the absorption of ammonia and nitrates by cryptogamic plants: by *A. B. Bineau*. Ann. Ch. Phys. [3] xlvi. 60.

—— Volumetric determination of nitrates by silver: by *C. Mohr*. Ann. Ch. Pharm. xcix. 197.

—— On basic mercuric nitrate: by *M. Ditten*. J. Pharm. [3] xxix. 160.

Nitre.—Formation of nitre in Hungary. Wien. geol. Jahrb. iii. 324, 453.

Nitre.—On the origin of nitre: by *M. Desmarest*. Compt. rend. xliii. 89, 316; Chem. Gaz. 1856, 330.

—— Note on two algæ which came into existence during the experiments of *M. Boussingault*, on the action of nitre on vegetation: by *M. Montagne*. Compt. rend. xlii. 756.

—— Contributions to the history of nitric acid, with especial reference to the valuation of nitre: by *F. A. Abel* and *C. L. Bloxam*. Chem. Soc. Qu. J. ix. 97.

—— Poisoning by nitre. J. Pharm. [3] xxix. 126.

—— On the so-called Austrian valuation of nitre, and on the detection of nitrate of soda in common nitre: by *F. Joel*. Ann. Ch. Pharm. c. 78.

Nitric oxide.—On the action of nitric oxide gas on anhydrous sulphuric acid: by *A. Brüning*. Ann. Ch. Pharm. xcviii. 377; Chem. Gaz. 1856, 301.

Nitrification.—Remarks on nitrification; by *C. F. Schönbein*. Phil. Mag. [4] xii. 457.

Nitrites.—On the action of sulphuric acid on the amides and nitriles: by *G. B. Buckton* and *A. W. Hofmann*. Chem. Soc. Qu. J. ix. 241; Proc. Roy. Soc. vii. 344, viii. 158; Chem. Gaz. 1856, 58, 305; Phil. Mag. [4] xi. 549; Ann. Ch. Phys. [3] xlvi. 366.

Nitrogen.—New method of estimating nitrogen in nitrates. Experiments showing that nitrate of potash is decomposed by plants, and that for an equal quantity of nitrogen, nitrate of potash acts more strongly than sal-ammoniac: by *G. Ville*. Compt. rend. xli. 938.

—— Researches on the distribution of nitrogenous matters in the various parts of the beet plant: by *J. Pierre*. Compt. rend. xlii. 715.

—— Experimental researches on nitrification, and on the source of nitrogen in plants: by *M. Cloez*. Compt. rend. xli. 935.

—— Researches on the assimilation of atmospheric nitrogen by plants: by *M. Harting*. Compt. rend. xli. 942.

—— Volumetric determination of nitrogen by silver: by *C. Mohr*. Ann. Ch. Pharm. xcix. 197.

—— On the action of the oxygen-compounds of nitrogen on iodide of potassium in presence of water: by *M. Béchamp*. Compt. rend. xliii. 388.

—— On a new series of organic acids containing nitrogen: by *E. Frankland*. Ann. Ch. Pharm. xcix. 342.

—— On the specific volumes of azotised compounds: by *H. Kopp*. Ann. Ch. Pharm. xcvii. 374; c. 19.

Nutrition.—Researches on the chemical composition and the nutritive equivalents of the food of man (cereals and leguminosæ): by *M. Poggiale*. Compt. rend. xliii. 370; J. Pharm. [3] xxx. 180, 255.

—— On the composition and nutritive value of certain residues of manufacturing processes, used as fodder in rural economy: by *H. Ritthausen*. J. pr. Chem. lxvi. 289.

I. Residue of the distillation of spirit from potatoes, p. 289.
II. Residue of the distillation of spirit from barley, p. 308.
III. Brewing residues, p. 311.

Nutrition.—On the use of horse-flesh as food: by *Is. Geoffroy St. Hilaire.* Compt. rend. xliii. 455.

Nux vomica.—On a new method of extracting the alkaloids contained in nux vomica without alcohol: by *J. Horsley.* Pharm. J. Trans. xvi. 179.

—— On powder of nux vomica: by *N. Gilles.* J. Pharm. [3] xxix. 220.

O.

Oak-galls.—English oak-galls: by *Dr. Vinen.* Pharm. J. Trans. xvi. 137.

Oil-painting.—Experimental researches on oil-painting: by *E. Chevreul.* Ann. Ch. Phys. [3] xlvii. 209.

Oils.—On a new substance called *wood-oil*, which may serve as a substitute for balsam of copaiba: by *D. Hanbury.* Pharm. J. Trans. xv. 321; J. Pharm. [3] xxix. 289.

—— On wood-oil: by *M. Guibourt.* J. Pharm. [3] xxx. 189.

—— Note on the oils used in the preparation of Turkey red: by *M. Pelouze.* Letter of *MM. Henry,* on Turkey red; Compt. rend. xlii. 1196.

—— Note on iodised oil: by *M. Hugouneng.* J. Pharm. [3] xxix. 214.

—— On sweet oil of wine: by *C. Blondeau.* J. Pharm. [3] xxix. 249, 344, 424.

—— On a new acid obtained by the oxidation of hydrate of oil of turpentine: by *J. Personne.* Ann. Ch. Pharm. c. 253.

—— Oil of cotton seed and oil of pignut hiccory. Pharm. J. Trans. xvi. 334.

—— On Egusé oil, a vegetable product from West Africa: by *W. F. Daniell.* Pharm. J. Trans. xvi. 307.

—— On the preparation of drying oil: by *R. Wagner.* Chem. Gaz. 1856, 437.

—— On para-nut oil: by *G. C. Caldwell.* Ann. Ch. Pharm. xcviii. 120.

Oils, Volatile.—The mutual action of chromic acid and the volatile oils: by *J. T. Plummer.* Pharm. J. Trans. xvi. 130.

—— On some processes relating to the analysis of essential oils: by *M. Berthelot.* J. Pharm. [3] xxviii. 450.

—— On the artificial production of oil of cinnamon. Compt. rend. xlii. 222; Chem. Gaz. 1856, 88.

—— On the essential oil contained in essence of madder: by *M. Jeanjean.* Compt. rend. xlii. 857; Remarks by *M. Biot,* ibid. 859.

—— On the essence of merbane, commonly called artificial essence of bitter almonds: by *M. Wagner.* J. Pharm. [3] xxviii. 486.

—— Artificial production of oil of mustard: by *Berthelot* and *De Luca.* Ann. Ch. Pharm. xcvii. 126.

—— Adulteration of oil of anise with alcohol: by *W. Procter.* J. Pharm. [3] xxix. 218.

Oils, Volatile.—Researches on the volatile oil of templin: by *M. Flückiger*. J. Pharm. [3] xxix. 39.

—— Researches on oil of turpentine; new acid obtained by the oxidation of hydrate of turpentine: by *M. Personne*. Compt. rend. xliii. 553; Chem. Gaz. 1856, 371.

—— Action of nitric acid upon oil of turpentine: by *L. Svanberg* and *F. L. Ekman*. J. pr. Chem. lxvi. 219.

—— Poisoning by vapours of turpentine: by *M. de Calvi*. Compt. rend. xli. 1041.

—— Action of turpentine-vapours when inhaled: by *M. Letelier*. Compt. rend. xlii. 243.

—— On the hydrates of oil of turpentine: by *M. Berthelot*. J. Pharm. [3] xxix. 28.

Ononis.—On the root of *Ononis spinosa*: by *H. Hlasiwetz*. J. pr. Chem. lxv. 419; Ann. Ch. Phys. [3] xlvi. 374.

Opium.—On certain constituents of opium: by *T. Anderson*. Ed. Phil. Trans. xxi. Pt. I. 204; Ann. Ch. Pharm. xcviii. 44; Chem. Soc. Qu. J. ix. 273.

—— Indigenous opium. Pharm. J. Trans. xv. 430.

Organic Compounds.—On the history of organic compounds containing metals: by *E. Frankland*. Ann. Ch. Pharm. xcix. 333.

Organo-metallic Bodies.—Researches on the organo-metallic bodies. Third Memoir. On a new series of organic acids containing nitrogen: by *E. Frankland*. Proc. Roy. Soc. viii. 198; Ann. Ch. Pharm. xcix. 342.

Organic Substances.—Testing of various organic substances with sulphuric acid and bichromate of potash: by *M. Eboli*. Chem. Gaz. 1856, 251.

Ostrich.—Analysis of the egg-shell of the ostrich: by *W. Wicke*. Ann. Ch. Pharm. xcvii. 350.

Oxalates.—On the oxalates: by *A. Vogel, Jun.* Bayer, Akad. Abhandl. 1855, 667.

—— On the oxalates of the alkalis and alkaline earths: by *A. Souchay* and *E. Lenssen*. Ann. Ch. Pharm. xcix. 31; Chem. Gaz. 1856, 385.

—— On oxalate of lime: by *E. E. Schmid*. Ann. Ch. Pharm. xcvii. 225.

—— On the solubility of oxalate of lime in phosphoric acid: by *C. Neubauer*. Ann. Ch. Pharm. xcix. 223.

Oxamates.—On the oxamates: by *P. J. Engström*. J. pr. Chem. lxviii. 433.

Oxides.—On the various methods of determining the basic power of an oxide (conclusion): by *H. Rose*. Pogg. Ann. xcvi. 550.

—— On the reduction of some oxides and chlorides by glucose: by *R. Böttger*. J. Pharm. [3] xxxix. 479.

Oxychlorides.—On the oxychlorides: by *W. Casselmann*. Ann. Ch. Pharm. xcviii. 213; Chem. Gaz. 1856, 364.

Oxygen.—Researches on oxygen in the nascent state: by *A. Houzeau*. Compt. rend. xliii. 34; Pogg. Ann. xcix. 165; J. Pharm. [3] xxx. 342.

—— On the relations between certain compounds differing by H_2 and O_2: by *Sterry-Hunt*. Compt. rend. xli. 1167.

Oxygen.—On the action of organic bodies upon oxygen: by *M. Phipson.* Compt. rend. xliii. 864.

—— On the condition of the oxygen absorbed into the blood during respiration: by *G. Harley.* Proc. Roy. Soc. viii. 78; Chem. Gaz. 1856, 196.

—— On the preparation of oxygen: by *G. Hornsby.* Pharm. J. Trans. xv. 352; also by *H. M. Witt,* ibid. 411, 503; also by *Mr. Brown,* ibid. 469; see further J. Pharm. [3] xxx. 46.

Ozone.—On the constitution and properties of ozone: by *T. Andrews.* Phil. Trans. 1856, i. 3; Chem. Soc. Qu. J. ix. 168; Ann. Ch. Pharm. xcvii. 371; Pogg. Ann. xcviii. 635; Ann. Ch. Phys. [3] xcvii. 181.

—— On the ozone-question: by *F. M. Baumert.* Pogg. Ann. xcix. 88.

—— Formation of ozone. Pogg. Ann. xcviii. 511.

—— On the quantity of ozone in the acid formed by the slow combustion of phosphorus in the air. Pogg. Ann. xcix. 478.

—— On the formation and sources of atmospheric ozone: by *M. Scoutetten.* Compt. rend. xliii. 93.

—— On atmospheric ozone; remarks on a recent communication by *M. Cloez:* by *M. Scoutetten.* Compt. rend. xliii. 216.

—— On the preparation of ozonised oxygen from oxide of silver: by *C. F. Schönbein.* J. pr. Chem. lxvi. 280.

—— Observations on ozone: by *M. Bineau.* Compt. rend. xliii. 162; Phil. Mag. [4] xi. 324.

—— On ozone, and ozonic actions, in mushrooms: by *C. F. Schönbein.* Phil. Mag. [4] xi. 137; J. pr. Chem. lxvii. 497.

—— On ozonised oxygen: by *C. F. Schönbein.* J. pr. Chem. lxvi. 286.

—— On iodide of potassium as a test for ozone: by *S. Cloez.* Compt. rend. xliii. 38; Phil. Mag. [4] xi. 237.

—— On the reaction of ozonised oil of turpentine and ether, on arsenic and antimony: by *C. F. Schönbein.* J. pr. Chem. lxvi. 272.

—— Influence of the proportion of ozone in the air on the sanitary condition of a country: by *M. Wolf.* Compt. rend. xlii. 944.

—— Ozonometric observations made with Schönbein's paper round the palace of St. Cloud: by *M. Berigny.* Compt. rend. xlii. 1115.

—— Ozone-observations in the year 1855: by *R. Wolf.* Pogg. Ann. xcvii. 640.

—— Remarks on the relative value of the ozonometers of Drs. Schönbein and Moffat: by *T. H. Barker.* Phil. Mag. [4] xi. 518.

—— On ozone-hydrogen: by *G. Osann.* Pogg. Ann. xcviii. 181.

P.

Painting.—Experimental researches on oil-painting: by *E. Chevreul.* Ann. Ch. Phys. [3] xlvii. 209.

Pancreatic Juice.—On the digestion and absorption of fatty substances without the aid of the pancreatic juice: by *M. Colin.* Compt. rend. xliii. 55.

Paraffin.—On paraffin: by *Fr. Filipuzzi.* J. pr. Chem. lxviii. 60; Wien. Akad. Ber. xvii. 425.

Peat.—On the products of the dry distillation of several varieties of peat and lignite: by *F. L. Sonnenschein.* J. pr. Chem. lxvii. 142.

—— Experiments made with a view to determine the comparative value of peat and peat-charcoal for agricultural purposes: by *E. W. Davy.* Phil. Mag. [4] xi. 172.

Pepsine.—On pepsine: by *M. Boudault.* J. Pharm. [3] xxx. 161.

Perfumes.—On the nature of perfumes, and on some flowers which might be cultivated in Algeria: by *M. Millon.* J. Pharm. [3] xxx. 281.

Phaseomannite.—On phaseomannite, a new kind of sugar contained in the unripe pods of *Phaseolus vulgaris:* by *H. Vohl.* Ann. Ch. Pharm. xcix. 125; Chem. Gaz. 1856, 331.

Phenyl.—Triphenylamine, a product of the decomposition of the acid sulphite of cinnamic aldehyde-ammonia: by *A. Gössmann.* Ann. Ch. Pharm. c. 57.

Phloretin.—On phloretin: by *H. Hlasiwetz.* Wien. Akad. Ber. xvii. 382: Chem. 1856, 81. J. pr. Chem. lvii. 105.

Phorone.—On phorone: by *L. Bodart.* Compt. rend. xliii. 394.

Phosphates.—On the influence of the proportion of phosphate of lime in the food on the formation of the callus: by *A. Milne-Edwards.* Compt. rend. xlii. 631.

—— On tribasic phosphate of soda: by *M. Groves.* J. Pharm. [3] xxix. 284.

—— On phosphate of soda and lithia, and the quantitative estimation of lithia: by *W. Mayer.* Ann. Ch. Pharm. xcviii. 193; Ann. Ch. Phys. [3] xlvii. 288.

—— Action of phosphate of soda on fluor-spar at a red heat: by *H. Briegleb.* Ann. Ch. Pharm. xcvii. 95; Chem. Gaz. 1856, 149.

—— On the earthy phosphates of the urine: by *C. Neubauer.* J. pr. Chem. lxvii. 65, 491; Chem. Gaz. 1856, 204.

—— On some ferroso-ferric phosphates: by *G. Jenzsch.* Pogg. Ann. xcviii. 629.

—— On blue ferroso-ferric phosphate: by *C. G. Wittstein.* Pogg. Ann. xcvii. 158.

—— On the manufacture of the superphosphates: by *A. Müller.* Chem. Gaz. 1856, 236.

—— On the superphosphate of decomposed bones: by *W. Wicke.* Ann. Ch. Pharm. xcix. 97; Chem. Gaz. 1856, 333.

—— On a new deposit of phosphate of lime: by *M. Mergy.* Compt. rend. xliii. 757.

Phosphides.—On metallic phosphides: by *H. Hvoslef.* Ann. Ch. Pharm. c. 99.

Phosphorescence.—See *Light.*

Phosphorus.—Improved process for the manufacture of phosphorus: by *Hugo Fleck.* Chem. Gaz. 1850, 279.

Phosphorus.—On the manufacture of phosphorus: by *M. Fleck.* J. Pharm. [3] xxx. 399.

—— On the crystalline form of phosphorus: by *E. Mitscherlich.* Pogg. Ann. xcviii. 547; J. pr. Chem. lxvi. 268; Ann. Ch. Phys. [3] xlvi. 308.

—— On phosphorus and its preparations: by *A. Chevalier* and *O. Henry.* Compt. rend. xlii. 341.

—— Detection of phosphorus in cases of poisoning: by *E. Mitscherlich.* J. Pharm. [3] xxix. 353; J. pr. Chem. lxvi. 238; Chem. Gaz. 1856, 115.

—— Action of red phosphorus on the animal economy: by *MM. Orfila* and *Rigout.* Compt. rend. xlii. 201; also by *A. Chevalier,* ibid. 272.

—— On the purification of amorphous phosphorus: by *E. Nicklès.* Compt. rend. xlii. 646; Chem. Gaz. 1856, 195; J. Pharm. [3] xxix. 334; Sill. Am. J. [2] xxii. 244.

—— On the action of pentachloride of phosphorus on the fixed acids which give rise to the formation of pyro-acids: by *L. Bodart.* Compt. rend. xlii. 391.

—— Researches on some new phosphuretted bases: by *A. Cahours* and *A. W. Hofmann.* Chem. Gaz. 1856, 10; Compt. rend. xliii. 1092.

—— On the compounds of phosphorus with ethyl: by *F. Berlé.* Ann. Ch. Pharm. xcvii. 334.

Photography.—On heliographic engraving on marble and lithographic stone: by *Niepce de St. Victor.* Compt. rend. xliii. 874, 912: Remarks by *M. Chevreul,* ibid. 914.

—— Photographic examination of the solar spectrum: by *W. Crookes.* Pogg. Ann. xcvii. 616.

—— On the method of preserving the sensitiveness of collodion plates: by *J. Spiller and W. Crookes.* Phil. Mag. [4] xi. 334.

—— Photographical experiments: by *C. H. L. v. Babo.* Pogg. Ann. xcvii. 499.

—— On the application of the light of sulphur or phosphorus burning in oxygen, to the production of photographs: by *R. Böttger.* J. pr. Chem. lxviii. 363. Pharm. J. Trans. xvi. 223.

—— Conditions of success and causes of failure in photography. Pharm. J. Trans. xv. 560.

—— New process of photographic engraving and printing: by *MM. Harville* and *Pont.* Compt. rend. xli. 966.

—— Transference of photographic pictures upon stone: by *M. Poitevin.* Compt. rend. xlii. 20.

—— On photographic iodide of lead: by *M. Roussieu.* Ann. Ch. Phys. [3] xlvii. 154.

Photometer.—See *Light.*

Pigments.—Composition of two mineral pigments: by *T. H. Rowney.* Ed. N. Phil. J. [N.S.] ii. 306.

Plants.—On the function of nitrates in the economy of plants: by *G. Ville.* Ann. Ch. Phys. [3] xlvi. 314; Compt. rend. xli. 987; xlii. 85, 612.

Plant-ash.—See *Ash.*

—— Researches on the assimilation of nitrogen by plants: by *M. Harting.* Compt. rend. xli. 942.

—— Experimental researches on nitrification, and on the source of nitrogen in plants: by *M. Cloez.* Compt. rend. xli. 935.

—— Experiments showing that nitrate of potash is decomposed by plants, and that for an equal quantity of nitrogen, nitrate of potash acts more strongly than sal-ammoniac: by *G. Ville.* Compt. rend. xli. 938.

—— Experimental researches on the relation of plants to atmospheric moisture. Part II.—Relation of plants to the water which moistens their aerial surface: by *M. Duchartre.* Compt. rend. xlii. 428, 790.

—— Experiments on the power of absorbing water possessed by the roots of aerial plants: by *M. Chatin.* Compt. rend. xlii. 841.

—— Experimental researches on the respiration of plants: by *M. Duchartre.* Compt. rend. xlii. 37.

—— On the distribution of inorganic elements in the principal families of the vegetable kingdom: by *MM. Malaguti* and *Durocher.* Compt. rend. xliii. 384, 482.

—— Method of preserving plants with their natural form, and the colour of their flowers: by *Reveil* and *Bergot.* J. Pharm. [3] xxx. 105.

—— Note on two algæ which came into existence in the course of M. Boussingault's experiments on the action of nitre on vegetation: by *M. Montagne.* Compt. rend. xlii. 756.

Platinum.—On a bed of platinum observed in a vein in the Province of Antioquia (New Granada): by *M. Boussingault.* Compt. rend. xlii. 917.

—— Platinum-ore from Borneo: by *Max Böcking.* J. pr. Chem. lxvii. 207.

—— On the crystallisation of platinum from fusion: by *J. W. Mallet.* Sill. Am. J. [2] xx. 340; Chem. Gaz. 1856, 14.

—— On the platinising of metals by the electric current: by *R. Böttger.* J. pr. Chem. lxviii. 369.

—— On the platinum-bases: by *Chr. Grimm.* Ann. Ch. Pharm. xcix. 67.

—— On the cyanides of platinum: by *A. Schafarik.* J. pr. Chem. lxvi. 385.

—— On the fluorescence of platinocyanide of potassium: by *R. Böttger.* Pogg. Ann. xcvii. 333.

—— A new platinum salt: by *Chr. Grimm.* Ann. Ch. Pharm. xcix. 95.

—— On some platino-cyanides: by *P. P. Weselsky.* Wien. Akad. Ber. xx. 282; Chem. Gaz. 1856, 443.

Poisons.—On the detection of poisons: by *F. J. Otto.* Ann. Ch. Pharm. c. 39.

Polarisation.—See *Light.*

Populin.—On populin: by *R. Piria.* Ann. Ch. Pharm. xcvi. 375.

Potash.—On the potash contained in the stems of Algerian tobacco. and on its use in the preparation of nitre: by *A. Commaillé.* J. Pharm. [3] xxix. 106.

—— On the preparation of hydrate of potash from nitre: by *A. Geuther.* Ann. Ch. Pharm. xcvii. 223; Chem. Gaz. 1856, 219.

Potassium.—On the magnetism and electric conductivity of potassium and sodium: by *M. Lamy*. Compt. rend. xliii. 693.

—— Combustion of potassium and sodium in oxygen gas: J. pr. Chem. lxvii. 172.

—— On the double salts of biniodate of potash with chloride of potassium and sulphate of potash: by *C. Rammelsberg*. Pogg. Ann. xcvii. 92.

—— Test for carbonate and iodate of potash in iodide of potassium: by *W. Copney*. Pharm. J. Trans. xv. 504; J. Pharm. [3] xxx. 119.

Propylene.—New mode of formation of propylene: by *L. Dusart*. Ann. Ch. Pharm. xcvii. 127.

—— On iodopropylene: by *Berthelot* and *De Luca*. Compt. rend. xlii. 233; Chem. Gaz. 1856, 171.

Propylenyl.—On some compounds of propylenyl (allyl or acryl): by *N. Zinin*. Ann. Ch. Pharm. xcvi. 361.

Pyroxylin.—Researches on pyroxylin: by *A. Béchamp*. Ann. Ch. Phys. [3] xlvi. 338.

Q.

Quercitrin.—On rutic acid and quercitrin: by *H. Hlasiwetz*. Wien. Akad. Ber. xvii. 375; Chem. Gaz. 1856, 106; J. pr. Chem. lxvii. 97.

R.

Radicals.—On a new class of organic radicals: by *A. Wurtz*. Ann. Ch. Pharm. xcvi. 364.

Radicals, organic.—On the preparation of the chlorides and bromides of the organic radicals, by the action of terchloride or terbromide of phosphorus, on the corresponding mono-hydrated acids: by *M. Béchamp*. Compt. rend. xlii. 224; Chem. Gaz. 1856, 164.

Resins.—Process for decolorising resins: by *M. Losh*. J. Pharm. [3] xxix. 465.

—— The gums and resins of commerce: by *P. L. Simmonds*. J. Fr. Inst. [3] xxxii. 177, 279.

Respiration.—On the condition of the oxygen absorbed into the blood during respiration: by *G. Harley*. Proc. Roy. Soc. viii. 78; Chem. Gaz. 1856, 196.

—— On the solubility of gases in saline solutions, with reference to the theory of respiration; by *M. Fernet*. Compt. rend. xli. 1237; Ann. Ch. Phys. [3] xlvii. 360.

—— Experimental researches on the respiration of plants: by *M. Duchartre*. Compt. rend. xlii. 37.

Rhatany.—On rhatany root: by *Dr. Schuchardt*. Pharm. J. Trans. xvi. 30, 132; also by *D. Hanbury*. J. Pharm. [3] xxx. 216.

Rhodanogen.—*See* Sulphocyanogen.
Rhubarb.—On the composition of rhubarb-juice: by *E. Kopp*. Compt. rend. xliii. 475.
Rocks.—Reply to the objections of M. Durocher, concerning granitic rocks: by *J. Fournet*. Compt. rend. xliii. 188.
Rotatory power.—See *Light*.
Rubian.—On rubian and its products of decomposition; Part III.: by *E. Schunck*. Phil. Mag. [4] xii. 200, 270.

S.

Saccharine substances.—On some saccharine substances: by *M. Berthelot*. Ann. Ch. Phys. [3] xlvi. 89.
—— On the compounds of saccharine substances with acids: by *M. Berthelot*. Ann. Ch. Phys. [3] xlvii. 297; Compt. rend. xlii. 1111.
Salicin.—Action of nitric acid on salicin: by *R. Piria*. Il Nuovo Cimento ii. 299; Ann. Ch. Phys. [3] xlvii. 114.
Salicyl.—On the salicyl-compounds: by *H. Limpricht*. Ann. Ch. Pharm. xcviii. 256; xcix. 249.
Saline solutions.—Sixth memoir on the supersaturation of saline solutions: by *H. Loewel*. General view of this research: by *M. Chevreul*. Compt. rend. xliii. 709.
Saliva.—On sulphocyanide of potassium, considered as one of the constant and normal constituents of the saliva: by *M. Longet*. Compt. rend. xlii. 480.
Salts.—On the crystalline form and chemical composition of certain salts: by *C. Marignac*. Ann. Min. [5] ix. 1.
—— Some experiments illustrative of the reciprocal decomposition of salts: by *J. H. Gladstone*. Chem. Soc. Qu. J. ix. 144.
—— On the causes of solubility of certain salt-atoms, and the boiling points of saturated solutions: by *P. Kremers*. Pogg. Ann. xcvii. 1.
—— Experiments on the relative solubility of saline mixtures: by *F. Pfaff*. Ann. Ch. Pharm. xcix. 224.
—— On the precipitation of various salts from solution: by *L. Margueritte*. Compt. rend. xliii. 50; Chem. Gaz. 1856, 334.
—— On the contractions which accompany the mixing of different saline solutions: by *P. Kremers*. Pogg. Ann. xcviii. 58.
—— On common salt and brine: by *M. Gouraux*. Compt. rend. xliii. 152.
—— On rock-salt and its origin in tertiary strata: by *M. Abich*. Compt. rend. xliii. 227.
—— On the crystalline form and composition of certain salts: by *C. Marignac*. Ann. Min. [5] ix. 1.
—— On neutrality in salts: by *M. Margueritte*. Ann. Ch. Phys. [3] xlviii. 355.
—— Precipitation of salts from solution. Pharm. J. Trans. xvi. 330.

Saponification.—See *Fats*.

Sarsaparilla.—On sarsaparilla: by *L. de Kernota*. J. Pharm. [3] xxix. 383.

Scarifiers.—On the materials for making scarifiers: by *B. Hambly*. Chem. Gaz. 1856, 97.

Schist.—On the products of the dry distillation of the Rhenish bituminous schist, and of Saxon and Thuringian lignite, with their application to purposes of illumination: by *H. Vohl*. Ann. Ch. Pharm. xcvii. 9.

Sea-weeds.—Experiments on certain sea-weeds of an edible kind: by *J. Davy*. Proc. Roy. Soc. Edinb. iii. 363.

Secretions.—On the nature of the liquid secreted by the abdominal gland of insects of the genus *Carabus*: by *M. Pelouze*. Compt. rend. xliii. 123. [Remarks on analogous secretions in other insects: by *M. Duméril*. Ibid. 125.] Chem. Gaz. 1856, 368.

Selenium.—On the crystalline form and isomeric modifications of selenium, and on the crystalline forms of iodine and phosphorus: by *E. Mitscherlich*. Pogg. Ann. xcviii. 547: Ann. Ch. Phys. [3] xlvi; J. pr. Chem. lxvi. 257.

—— On the isomeric modifications of selenium: by *V. Regnault*. Pogg. Ann. xcviii. 396; Ann. Ch. Phys. [3] xlvi. 257.

—— On selenmethyl: by *F. Wöhler* and *J. Dean*. Ann. Ch. Pharm. xcvii. 5; Sill. Am. J. [2] xxi. 247.

Sewers.—On the alkaline emanations from sewers and cesspools: by *W. Odling*. Guy's Hospital Reports [3] ii. 245.

Shells.—On the shells of the mollusca, the byssus, and the chitin question: by *J. Schlossberger*. Ann. Ch. Pharm. xcviii. 99; Chem. Gaz. 1856, 327.

Silica.—On the non-existence of polarising silica in the organic kingdoms: by *J. W. Bailey*. Sill. Am. J. [2] xxi. 357.

—— On hydrate of silica, and the formation of opal and quartz: by *O. Maschke*. J. pr. Chem. lxviii. 233.

—— On the solubility of silica: by *H. Ludwig*. Arch. Pharm. cxxxiv. 129: Chem. Gaz. 1856, 45.

Silicates.—Theoretical view of the intervention of alkaline silicates in the artificial formation of hydraulic limestones, cements, and silicious lime-stones, with some geological considerations on formation, by the humid way in general: by *M. Kuhlmann*. Compt. rend. xli. 1029.

Silicium.—On silicium: by *F. Wöhler*. Pogg. Ann. xcvii. 484; Ann. Ch. Phys. [3] xlvii. 116; Ann. Ch. Pharm. xcvii. 266.

—— On a new mode of obtaining silicium: by *F. Wöhler*. Compt. rend. xlii. 48; Chem. Gaz. 1856, 91.

—— On crystallised silicium and carbon: by *H. Ste.-Claire Deville*. Compt. rend. xlii. 49, 1313; Chem. Gaz. 1856, 101.

—— On the crystalline form of silicium: by *H. de Senarmont*. Ann. Ch. Phys. [3] xlvii. 169.

—— Crystalline form of silicium. Pogg. Ann. xcvii. 644.

—— On the formulæ of silicium and titanium compounds: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 265.

Silk.—On the decoloration of silk and wool dyed with picric acid: by *C. Pugh*. J. pr. Chem. lxv. 368; Chem. Gaz. 1856, 297.

Silk.—On the presence of lime in silk, and the inconvenience which it produces in the operation of cleansing: by *M. Guinon*. Compt. rend. xlii. 239.

Silver.—On the formation of crystallised sulphocyanide (rhodanide) of silver: by *A. Gössmann*. Ann. Ch. Pharm. c. 76.

—— New process for gilding and silvering metals: by *C. Guerin*. Compt. rend. xliii. 808.

—— On iodide of silver and the metallic fluorides: by *H. Ste.-Claire Deville*. Compt. rend. xliii. 970.

—— On the extraction of silver from its ores in the wet way: by *A. Patera*. Wien. geol. Jahrb. iii. 573.

—— On the treatment of the rich silver ores of Joachimsthal in Bohemia: by *A. Patera*. Ann. Min. [5] viii. 68: Geol. Soc. Qu. J. xii. Part. II. 6; Chem. Gaz. 1856, 274.

—— History and description of the ores and foundries of lead, copper, and silver of Lozère. Ann. Min. [5] vii. 1: viii. 351.

—— On the extraction of the silver and lead from the argentiferous galena of Pribram, Bohemia: by *M. Kleszczynsky*. Geol. Soc. Qu. J. xii. pt. ii. 17.

—— Reduction of silver: by *J. Wiggin*. Pharm. J. Trans. xv. 322.

—— On the reduction of silver: J. Pharm. [3] xxix. 362.

—— Preparation of pure silver from silver containing copper: by *W. Wicke*. Ann. Ch. Pharm. xcviii. 143; Chem. Gaz. 1856, 211.

—— On the causes of the serious loss of silver which occasionally takes place during the roasting of silver ores: by *Prof. Plattner*. Chem. Gaz. 1856, 152.

—— On the loss of silver by capellation: by *B. Hambly*. Chem. Gaz. 1856, 185.

—— Report on a memoir by M. Jules Barse on a method of distinguishing, by special reactions, silicium and tungsten from silver: by *M. Balard*. Compt. rend. xli. 1069.

—— On the silvering and gilding of glass: by *J. Liebig*. Ann. Ch. Pharm. xcviii. 132; Chem. Gaz. 1856, 213.

—— Action of hydriodic acid on silver: by *H. Ste.-Claire Deville*. Compt. rend. xlii. 894; Chem. Gaz. 1856, 244.

—— On the composition of fulminating silver: by *O. B. Kuhn*. Chem. Gaz. 1856, 189.

—— A salt which gives off ammonia when treated with hydrochloric acid. Ann. Ch. Pharm. xcvii. 18.

Skin.—Experimental researches on the question "Whether water and dissolved substances are absorbed by the skin:" by *M. Poulet*. Compt. rend. xlii. 435.

Slags.—On the composition of bank-note slag: by *F. W. Griffin*. Pharm. J. Trans. xv. 353, 432.

Soap.—Improvement in the preparation of soap: Pharm. J. Trans. xvi. 331.

Soda.—On the discovery of artificial soda: by *M. Dumas*. Compt. rend. xlii. 553.

—— Processes for obtaining sulphate of soda, soda, and sulphuric acid: by *L. Margueritte*. Chem. Gaz. 1856, 51.

—— Purification of soda from sulphur. Polyt. J. cxi. 370. Pharm. J. Trans. xvi. 222.

Soda.—On an improved method of manufacturing artificial soda and sulphuric acid: by *E. Kopp*. Ann. Ch. Phys. [3] xlviii. 81.

—— On phosphate of soda and lithia, and the quantitative determination of lithia: by *W. Mayer*. Ann. Ch. Pharm. xcviii. 193; Ann. Ch. Phys. [3] xlvii. 288.

Sodium.—On the position of sodium in the thermo-electric scale: by *G. Gore*. Pharm. J. Trans. xvi. 321.

—— On sodium and its manufacture. J. Fr. Inst. [3] xxxi. 39.

—— On the preparation of sodium and aluminium: by *H. Ste.-Claire Deville*. Ann. Ch. Phys. [3] xlvi. 415.

—— Combustion of sodium and potassium in oxygen gas. J. pr. Chem. lxvii. 172.

—— On the magnetism and electric conductivity of potassium and sodium: by *M. Lamy*. Compt. rend. xliii. 693.

——Explosive action of sodium on water: by *F. W. Griffin*. Phil. Mag. [4] xii. 78.

—— On a double hyposulphate of sodium and copper: by *W. Schütte*. Compt. rend. xlii. 1267; Chem. Gaz. 1856, 351.

—— On the transformation of fluoride of aluminium and sodium into aluminate of soda: by *C. Tissier*. Compt. rend. xliii. 102; Chem. Gaz. 1856, 344.

Soils.—On the analysis of some vegetable soils with a view to their amelioration: by *M. Mengy*. Ann. Min. viii. 513.

Solanine.—On solanine and its derivatives: by *M. Moitessier*. Compt. rend. xliii. 978.

Solubility of salts.—On the curves of solubility of certain salt-atoms, and the boiling points of saturated saline solutions: by *P. Kremers*. Pogg. Ann. xcix. 25.

Spheroidal state.—On the rotation of a body in the spheroidal state round a fixed point: by *M. Boutigny*. J. Pharm. [3] xxxix. 355.

Starch.—On the products of the transformation of starch and lignin under the influence of alkalis, chloride of zinc, and acids: by *M. Béchamp*. Compt. rend. xlii. 1210.

—— Researches on the formation of starch and lignin under the influence of alkalis, chloride of zinc, and acids: by *A. Béchamp*. Ann. Ch. Phys. [3] xlviii. 458.

—— The starch of *Fritillaria imperialis* as a substitute for potato-starch. Pharm. J. Trans. xv. 564.

Stearoptene.—On the stearoptene of *Ledum palustre*: by *M. Buchner*. J. Pharm. [3] xxix. 318.

Steel.—New mode of manufacturing iron and steel without fuel: by *H. Bessemer*. Chem. Gaz. 1856, 336.

—— Improvements in the manufacture of cast steel (Price and Nicholson's patent.) Chem. Gaz. 1856, 300.

—— Improvements in the process of manufacturing cast steel (F. Uchatius' patent.) Chem. Gaz. 1856, 358.

—— Manufacture of steel by electricity. J. Fr. Inst. [3] xxxi. 248.

Stibethyl, Stibamyl, &c.—*See* Antimony.

Stoïchiometry.—Contributions to the stoïchiometry of the physical properties of chemical compounds: by *H. Kopp*. Ann. Ch. Pharm. c. 19.

VI. On the specific volumes of azotised compounds.

Stone.—Artificial stone: by *F. Kuhlmann.* J. Fr. Inst. [3] xxx. 221.
—— On the colouring of stone. J. Fr. Inst. [3] xxxi. 36.
Strontium.—On the iodides of barium and strontium: by *H. Croft.* Chem. Gaz. 1856, 125.
Strychnine.—On strychnine: by. *S. Macadam.* Pharm. J. Trans. xvi. 120, 160; J. Pharm. [3] xxx. 297.
—— On the action of urari and strychnine on the animal economy: by *A. Kölliker.* Proc. Roy. Soc. viii. 201.
—— Experimental researches on the action of strychnine upon the spinal marrow: by *G. Harley.* Compt. rend. xliii. 470.
—— Antidote for strychnine. J. Pharm. [3] xxix. 132.
—— Note on the detection of strychnine: by *Marshall Hall.* Pharm. J. Trans. xv. 376.
—— On the detection of strychnine by the formation of iodostrychnine: by *W. B. Herapath.* Proc. Roy. Soc. viii. 149; Chem. Gaz. 1856, 394.
—— Testing for strychnine, brucine, &c.: by *J. Horsley.* Pharm. J. Trans. xvi. 177, 179, 181.
—— Test for strychnine: by *J. W. Slater.* Pharm. J. Trans. xv. 520.
—— On the bichromate of potash and sulphuric acid test for strychnine: by *C. W. Bingley.* Chem. Gaz. 1856, 229.
Styracine.—Advantageous method of preparing styracine. Ann. Ch. Pharm. xcix. 376.
Subrenal capsules.—On certain reactions peculiar to the substance of the subrenal capsules: by *M. Vulpian.* Compt. rend. xliii. 663.
Sugar.—On a new method of extracting sugar from all plants: by *E. J. Maumené.* Ann. Ch. Phys. [3] xlviii. 23; J. Pharm. [3] xxx. 354.
—— On a new method of manufacturing sugar from beet-root or other saccharíferous plants: by *E. Pfeiffer.* Chem. Gaz. 1856, 154.
—— On the cause of the variation of rotatory power in starch-sugar, and on the probable existence of two varieties of amorphous glucose: by *M. Béchamp.* Compt. rend. xli. 896.
—— On the variable rotatory power of the mamellated glucose obtained from the grape: by *M. Dubrunfaut.* Compt. rend. xli. 739.
—— On inverted sugar: by *M. Dubrunfaut.* Compt. rend. xlii. 896.
—— On the reduction of some oxides and chlorides by glucose: by *R. Böttger.* J. Pharm. [3] xxix. 479.
—— On the variation of rotatory power in starch-sugar: by *M. Béchamp.* Compt. rend. xlii. 640.
—— Action of alkalis on sugar in the animal economy: by *M. Poggiale.* Compt. rend. xlii. 198; J. Pharm. [3] xlvi. 179.
—— On the solubility of lime in an aqueous solution of cane-sugar: by *M. Berthelot.* Ann. Ch. Phys. [3] xlvi. 173.
—— On sugar of milk: by *Staedeler* and *Krause.* Arch. Pharm. lxxxviii. 311; J. Pharm. [3] xxviii. 483.
—— On sugar of milk: by *L. Pasteur.* Compt. rend. xlii. 347. Remarks by *M. Biot.* Ibid. 351.
—— Note on sugar of milk: by *M. Dubrunfaut.* Compt. rend. xlii. 228.
—— Examination of two sugars (panoche and pure sugar) from California: by *S. W Johnson.* Sill. Am. J. [2] xxii. 6.

Sugar.—Researches on milk-sugar: by *A. Lieben.* J. pr. Chem. lxviii. 407.

—— Volumetric estimation of milk-sugar by Soleil's saccharimeter; and determination of the richness of milk: by *M. Poggiale.* J. Pharm. [3] xxx. 321.

—— On phaseomannite, a new kind of sugar contained in the unripe pods of *Phaseolus vulgaris*: by *H. Vohl.* Ann. Ch. Pharm. xcix. 125; Chem. Gaz. 1856, 331.

—— On the detection of sugar in the blood of the vena porta: by *M. Lehmann.* J. Pharm. [3] xxviii. 449. Remarks by *M. Bernard*, ibid.

—— Remarks on M. Lehmann's memoir on the detection of sugar in the blood of the vena porta: by *L. Figuier.* J. Pharm. [3] xxix. 96.

—— On physiological glycosury: by *H. Blot.* Compt. rend. xliii. 676.

Sulphates.—Note on the solubility of sulphate of baryta in hydrochloric acid: by *H. M. Noad.* Chem. Soc. Qu. J. ix. 15.

—— On the solution of sulphate of baryta in certain acid liquors: by *F. C. Calvert.* Proc. Roy. Soc. vii. 532; Chem. Gaz. 1856, 55; J. Pharm. [3] xxx. 86.

—— Sulphate of magnesia, manganous oxide, and zinc-oxide, a new conjugated salt: by *H. Vohl.* Ann. Ch. Pharm. xcix. 124.

—— On the substitution of native sulphate of magnesia for sulphuric acid in the manufacture of sulphate of soda and of hydrochloric acid: by *R. de Luna.* Ann. Ch. Phys. [3] xlvii. 176.

—— On sulphate of nickel: by *C. Marignac.* Ann. Ch. Pharm. xcvii. 294; Chem. Gaz. 1856, 260.

—— On the use of bisulphate of potash in the preparation of graduated solutions: by *E. Hubert.* J. Pharm. [3] xxx. 90.

—— Double salt of sulphate of potash with biniodate of potash: by *C. Rammelsberg.* Pogg. Ann. xcvii. 92.

—— Processes for obtaining sulphate of soda, soda, and sulphuric acid: by *L. Margueritte.* Chem. Gaz. 1856, 51.

Sulphides.—On the use of sulphide of carbon as a means of extracting the fat from bones, and the oil of oleagenous seeds, and for the cleansing of wool: by *M. Deiss.* Compt. rend. xlii. 207; Chem. Gaz. 1856, 136.

—— Application of sulphide of carbon. Pharm. J. Trans. xv. 517.

—— Action of nascent hydrogen on sulphide of carbon: by *A. Girard.* Compt. rend. xliii. 396.

—— On the decoloration of solution of indigo and tincture of litmus by bisulphide of hydrogen; by *C. F. Schönbein.* J. pr. Chem. lxvi. 270.

—— On a mode of formation of sulphide of iron: by *M. Chevreul.* Compt. rend. xliii. 128.

—— New methods of assaying the sulphides of lead and antimony: by *A. Levol.* Ann. Ch. Phys. [3] xlvi. 472; Chem. Gaz. 1856, 353.

—— On the behaviour of sulphide of mercury with the sulphides of the alkali-metals: *R. Weber.* Pogg. Ann. xcvii. 76.

Sulphobenzide.—On sulphobenzide: by *H. Gericke*. Ann. Ch. Pharm. c. 207; abstr. Ann. Ch. Pharm. xcviii. 319; Chem. Gaz. 1856, 308.

Sulphocyanogen.—On some sulphocyanogen compounds: by *C. Claus*. Ann. Ch. Pharm. xix. 48; Chem. Gaz. 1856, 344.

—— On sulphocyanide (rhodanide) of potassium: by *O. Nöllner*. Pogg. Ann. xcviii. 189.

—— On sulphocyanide of benzoyl: by *H. Limpricht*. Ann. Ch. Pharm. xcix. 117; Chem. Soc. Qu. J. ix. 264; Chem. Gaz. 1856, 351.

Sulphocyanides.—Preliminary notice on sulphocyanide of ethylene: by *H. L. Buff*. Ann. Ch. Pharm. xcvi. 302; J. Pharm. [3] xxix. 159.

Sulphomethylates.—On the action of water upon certain sulphomethylates: by *A. H. Church*. Phil. Mag. [4] xi. 68.

Sulphovinates.—On the sulphovinates; and on amylophosphoric acid and the amylophosphates: by *F. Guthrie*. Chem. Soc. Qu. J. ix. 131.

Sulphur.—On the allotropic states of sulphur: by *G. Magnus*. Pogg. Ann. xcix. 145.

—— On the modifications of sulphur under the influence of heat, and on its solvents: by *Ch. Ste-Claire Deville*. Ann. Ch. Phys. [3] xlvi. 94.

—— On red and black sulphur: by *G. Magnus*. Ann. Ch. Phys. [3] xlvii. 194.

—— On a blue modification of sulphur: by *J. Vogel, Jun.* J. Pharm. [3] xxix. 433.

—— On the red colouring of sulphur. J. pr. Chem. lxvii. 369.

—— New observations on soft sulphur: by *E. Baudrimont*. Compt. rend. xlii. 808; Chem. Gaz. 1856, 206; J. Pharm. xxix. 434.

—— On various tests for sulphur: by *C. Brame*. Compt. rend. xliii. 33.

—— New method for detecting the presence of sulphur in hops: by *R. Wagner*. Chem. Gaz. 1856, 134.

—— Effects of the presence of sulphur in coal gas: by *F. W. Griffin*. Pharm. J. Trans. xvi. 166.

—— On sulphurous baths: by *E. Soubeiran*. J. Pharm. [3] xxix. 161.

—— Remarks on the estimation of sulphur in iron, and on the solidity of sulphate of baryta in nitric acid: by *E. C. Nicholson* and *D. S. Price*. Phil. Mag. [4] xi. 169.

—— New process for the quantitative determination of sulphur in mineral waters: by *Maxwell Lyte*. Compt. rend. xliii. 765.

—— On the action of chloride of sulphur on formiate of baryta, acetate of soda, and benzoate of soda: by *W. Heintz*. Pogg. Ann. xcviii. 458.

Sulphuretted Hydrogen.—Apparatus for evolving sulphuretted hydrogen: by *M. Rissler*. J. Pharm. [3] xxx. 219.

—— Influence of hydrochloric acid on the precipitation of metals by sulphuretted hydrogen: by *M. Martin*. J. pr. Chem. lxvii. 371; Chem. Gaz. 1856, 311.

—— Effects of the presence of sulphur in coal gas. Pharm. J. Trans. xvi. 323.

Sulphuretted Hydrogen.—On the production of fluorescence by the flame of sulphuretted hydrogen: by *MM. v. Babo* and *Müller*. Chem. Gaz. 1856, 243.

T.

Tagala.—On extract of tagala: by *J. Cloquet*. J. Pharm. [3] xxx. 299.
Tantalum.—On tantalum and its compounds: by *H. Rose*. Berl. Akad. Ber. 1856, 385; Chem. Gaz. 1856, 421.
—— On tantalum and its compounds with chlorine and bromine: by *H. Rose*. Pogg. Ann. xcix. 65; Ann. Ch. Pharm. c. 242.
—— On the compounds of tantalum with fluorine: by *H. Rose*. Pogg. Ann. xcix. 481.
Tar.—On Burmese naphtha or Rangoon tar: by *Warren de la Rue* and *Hugo Müller*. Proc. Roy. Soc. viii. 221; Chem. Gaz. 1856, 375.
Taurin.—Occurrence of taurin in the tissue of the lungs: by *A. Cloetta*. Chem. Gaz. 1856, 61.
Tellurium.—On telluramyl and selenmethyl: by *F. Wöhler* and *J. Dean*. Ann. Ch. Pharm. xcvii. 1; Sill. Am. J. [2] xxi. 245.
Textile Fabrics.—On a new mode of conditioning all sorts of textile fabrics: by *M. Billard*. Compt. rend. xliii. 868.
Theine.—Determination of theine in guarana: by *J. Stenhouse*. Pharm. J. Trans. xvi. 312.
Thialdine.—On the crystalline form of thialdine and some of its salts: by *C. Rammelsberg*. Pogg. Ann. xcviii. 605.
Thymol.—Note on the derivatives of thymol, and on the preparation of biformene, a homologue of marsh-gas: by *M. Lallemand*. Compt. rend. xliii. 375; Report by *M. Bussy*, ibid, 459.
Tin.—On the electrical relations of tin and iron in various liquids: by *G. Gore*. Pharm. J. Trans. xv. 357.
—— On the action of tin on the blue colour of violets: by *M. Argillis*. J. Pharm. [3] xxx. 194.
Titanium.—On the formulæ of silicium and titanium compounds: by *H. Kopp*. Ann. Ch. Pharm. xcviii. 265.
—— On the bromide of titanium: by *F. B. Duppa*. Proc. Roy. Soc. viii. 42; Chem. Gaz. 1856, 138; Phil. Mag. [4] xii. 232; Ann. Ch. Phys. [3] xlvii. 164; Remarks by *H. Kopp*, ibid. 166.
—— On bromide of titanium: by *A. W. Hofmann*. Pogg. Ann. xcvii. 510; Compt. rend. xlii. 352.
—— On a titaniferous peridote from Pfanders in the Tyrol: by *A. Damour*. Compt. rend. xli. 1151; Ann. Min. [5] viii. 90.
Trimethylamine.—See *Methyl*.
Triphenylamine.—See *Phenyl*.
Tungsten.—Researches on tungsten and some of its compounds: by *M. Riche*. Compt. rend. xlii. 203; Chem. Gaz. 1856, 144.
Turpentine.—See *Oils*.

Type.—An improved manufacture of metallic alloy applicable to the casting of type (R. Besley's patent). Chem. Gaz. 1856, 219.

Types.—On the chemical type ammonia: by *A. W. Hofmann.* Pharm. J. Trans. xvi. 224.

U.

Ultramarine.—On the constitution of blue and green ultramarine: by *E. Breunlin.* Ann. Ch. Pharm. xcvii. 295; Phil. Mag. [4] xi. 528; Ann. Ch. Phys. [3] xlviii. 64.

—— On artificial ultramarine: by *C. Stölzel.* Ann. Pharm. xcvii. 35; Chem. Gaz. 1856, 91; J. Pharm. [3] xxix. 233. Also by *H. Wilkens.* Ann. Ch. Pharm. xcix. 21.

Uranium.—Note on the preparation of uranium: by *E. Peligot.* Compt. rend. xlii. 73; Chem. Gaz. 1856, 74; Pogg. Ann. xcvii. 630; J. Pharm. [3] xxix. 203; Ann. Ch. Pharm. xcvii. 253.

Urari.—On the action of urari and strychnine on the animal economy: by *A. Kölliker.* Proc. Roy. Soc. viii. 201.

Urea.—On two new artificial modes of formation of urea: by *J. Natanson.* Ann. Ch. Pharm. xcviii. 287; Ann. Ch. Phys. [3] xlviii. 309; Chem. Gaz. 1856, 293.

—— On some compounds of urea with organic acids: by *H. Hlasiwetz.* Wien. Akad. Ber. March, 1856; Chem. Gaz. 1856, 321.

——On the transformation of albuminoid substances into urea: by *A. Bêchamp.* Ann. Ch. Phys. [3] xlviii. 348; Ann. Ch. Pharm. c. 247.

——On the quantity of urea in diabetic urine: by *E. E. Schmid.* J. pr. Chem. lxvii. 315.

Ureas.—On the formulæ of some amides and ureas; and on the possibility of the artificial formation of creatine and creatinine: *C. Weltzien.* Ann. Ch. Pharm. c. 191.

Urine.—On the earthy phosphates of the urine: by *C. Neubauer.* J. pr. Chem. lxvii. 65; Chem. Gaz. 1856, 204.

—— On the volatile acids produced in the fermentation of diabetic urine: by *C. Neubauer.* Ann. Ch. Pharm. xcvii. 129; J. Pharm. [3] xxix. 320.

—— New method of determining iron in the urine by means of permanganate of potash: by *Dr. Böcker.* Chem. Gaz. 1856, 253.

—— Trimethylamine in human urine: by *V. Dessaignes.* Compt. rend. xliii. 670; Ann. Ch. Pharm. c. 218.

—— On physiological glycosury: by *H. Blot.* Compt. rend. xliii. 676.

Ursone.—On the composition of ursone: by *H. Hlasiwetz.* J. Pharm. [3] xxx. 398.

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Valerates.—On the valerate of ammonia: by *M. Laboureur.* J. Pharm. [3] xxx. 350.

Vanadium.—On the crystalline form and composition of native vanadiate of lead: by *C. Rammelsberg.* Pogg. Ann. xcviii. 249; J. pr. Chem. lxviii. 247.

—— On the composition of vanadite: by *A. Kenngott.* Pogg. Ann. xcix. 95.

Vapours.—On the application of a modification of Gay-Lussac's method of determining vapour-densities to substances of high boiling point: by *J. Natanson.* Ann. Ch. Pharm. xcviii. 301.

Vegetable Products.—Results of the examination of certain vegetable products from India: by *J. Stenhouse.* Part. I., Phil. Trans. 1856, i. 141; Ann. Ch. Pharm. xcviii. 166, 307; abstr. Chem. Soc. Qu. J. ix. 226; Proc. Roy. Soc. vii. 536; Chem. Gaz. 1856, 38; Phil. Mag. [4] xii. 59.

Vegetation.—Researches on vegetation: by *M. Boussingault.* Ann. Ch. Phys. [3] xlvi. 5, 225; J. Pharm. [3] xxix. 274.

Veratrine.—Toxicological and pharmaco-dynamical researches on veratrine: by *Dr. von Praag.* J. Pharm. [3] xxix. 56.

Vermilion.—On antimonial vermilion: by *E. M. Plessy.* Chem. Gaz. 1856, 103.

Violets.—On the action of tin on the blue colour of violets: by *M. Argillis.* J. Pharm. [3] xxx. 194.

Volcanoes.—On the volcanic phenomena of southern Italy: by *Ch. Ste-Claire Deville.* Compt. rend. xli. 62, 593; xlii. 1167; xliii. 204, 431, 359, 523, 606, 681, 745.

——On volcanic emanations: by *Ch. Ste.-Claire Deville.* Compt. rend. xliii. 955.

Volume.—On the specific volumes of azotised compounds: by *H. Kopp.* Ann. Ch. Pharm. xcvii. 374; c. 19.

——On the modification of the mean volume of certain salt-atoms and their solutions: by *P. Kremers.* Pogg. Ann. xcix. 446.

W.

Washing Bottle.—Description of a self-acting washing bottle: by *W. S. Clark.* Chem. Soc. Qu. J. ix. 200.

Water.—On the polar decomposition of water by common and atmospheric electricity: by *P. Andrews.* Pogg. Ann. xcix. 493.

Water.—On the decomposition of water by very weak electric currents, especially by machine electricity: by *H. Buff*. Ann. Ch. Pharm. xcvi. 257.

—— On Regnault's determination of the weight of a litre of air, and on the density of water at 0° C: by *R. Kohlrausch*. Pogg. Ann. xcviii. 178.

—— Experiments on the power of absorbing water possessed by the roots of aerial plants: by *M. Chatin*. Compt. rend. xlii. 841.

—— On the peculiar power possessed by porous media (sand and charcoal) of removing matter from solution in water: by *H. M. Witt*. Phil. Mag. [4] xi. 23.

—— On the action of water upon glass: by *J. Pelouze*. Compt. rend. xliii. 117; Chem. Gaz. 1856, 341.

—— On the action of sea-water on hydraulic compounds in general: by *M. Vicat*. Compt. rend. xlii. 1200.

—— Process for purifying water, and preventing incrustation in steam-boilers: by *W. Dantec*. Pharm. J. Trans. xv. 317.

—— Purification of water supplied to towns: Pharm. J. Trans. xv. 553.

—— Does a mineral water experience diurnal variations in its composition? by *E. Baudrimont*. J. Pharm. [3] xxix. 337.

—— New method of determining the proportion of matter dissolved in soft waters and rivers: by *MM. Boutron* and *Boudely*. J. Pharm. [3] xxx. 18.

—— Researches on the azotised products of sulphuretted thermal waters: by *J. Bouis*. Compt. rend. xli. 1161.

—— On the presence of ammonia in certain mineral waters: by *J. Bouis*. Compt. rend. xlii. 1269.

—— On mineral waters containing iodine: by *A. Erdmann* and *E. W. Olbers*. Ofversigt af. Kongl. Vetenskaps-akademiens Förhandlingar 1855, 81.

—— Detection of iodine in mineral waters: by *J. Liebig*. Ann. Ch. Pharm. xcviii. 51; Ann. Ch. Phys. [3] xlvii. 193; Chem. Gaz. 1856, 212.

—— On the natural mineral waters of Algeria: by *J. Oliffe*. J. Pharm. [3] xxix. 283.

—— The mineral springs of Brückenau, in Bavaria, containing butyric, propionic, acetic, and formic acids: by *Dr. Scherer*. Ann. Ch. Pharm. xcix. 257.

—— On the thermal springs of Carlsbad: by *Dr. Hochstetter*. Geol. Soc. Qu. J. xii. pt. II. 18.

—— Analysis of the water of the Dead Sea, taken in June, 1854: by *F. Moldenhauer*. Ann. Ch. Pharm. xcvii. 357.

—— Analysis of the mineral water at Guldhof, near Selowitz, in Mahren: by *F. Osnaghi*. Wien. Akad. Ber. xvii. 443.

—— Influence of the inundation of the Loire on the chemical composition of its waters: by *A. Bobierre*. Compt. rend. xliii. 400.

—— On the source of the water of the deep wells in the chalk under London: by *D. Campbell*. Chem. Soc. Qu. J. ix. 21.

—— Chemical examination of certain lakes and springs on the Turko-Persian frontier, near Mount Ararat: by *H. M. Witt*. Phil. Mag. [4] xi. 257.

Water.—Note on a mineral water from Frais-Vallon, near Algiers, and on the use of the mineral waters of Algeria: by *M. Millon.* J. Pharm. [3] xxix. 5.

—— On the variations which appear to take place in the composition of the water of the Dead Sea: by *M. Boussingault.* Compt. rend. xlii. 1230.

—— On the thermal waters of Nauheim: by *M. Ratureau.* Compt. rend. xlii. 438.

—— Analysis of the mineral waters of Neuhaus: by *J. Liebig.* Ann. Ch. Pharm. xcviii. 350.

—— New analysis of the mineral water of the saline and ferruginous springs of Plombières (Conclusion): by *O. Henry.* J. Pharm. [3] xxviii. 408.

—— Examination of the Rakoczy, Pandur, and Maxbrunnen waters at Kissingen: by *J. Liebig.* Ann. Ch. Pharm. xcviii. 145.

—— Analysis of a new mineral spring at Robetsch. Wien. geol. Jahrb. vi. 39.

—— New analysis of the iodo-bromuretted mineral water of Saxon (Valais): by *O. Henry.* J. Pharm. [3] xxx. 172, 246.

—— Analysis of the Schmökser water: by *A. W. Scherfel.* Wien. Akad. Ber. xvii. 449.

—— Analysis of two salt-springs from the Spessart: by *F. Moldenhauer.* Ann. Ch. Pharm. xcvii. 353.

—— Chemical examination of the mineral waters at Steben, in the Langenau, in the Bavarian Voigtland: by *E. v. Gorup-Besanez.* Acad. Cas. Leop.-Carol. Nat. Cur. N. acta. xxv. 1.

—— On the mineral springs of Szliáes, in Upper Hungary: by *A. Hauch.* Wien. geol. Jahrb. 1855, 314.

—— On the variations in the chemical composition of the Thames water during the year between May, 1855, and May, 1856: by *H. M. Witt.* Phil. Mag [4] xii. 114.

—— Analysis of spring-water at Vienna: by *M. Pohl.* Wien. Akad. Denschr. xv. 303.

—— Analysis of water from a volcanic lake. J. pr. Chem. lxvii. 249.

—— On the composition of a coloured liquid which is formed in a grotto of the village of Virtud, and gives rise to a small rivulet, known by the name of "River of Blood" (Rio de Sangre), near Cholateca (Central America): by *J. Rossignon.* Compt. rend. xliii. 680.

—— On the subterraneous waters of Provence: by *M. de Villeneuve-Flayosc.* Compt. rend. xliii. 1032.

—— New process for the quantitative determination of sulphur in mineral waters: by *Maxwell Lyte.* Compt. rend. xliii. 765.

—— Table of the specific gravity of sea-water: by *W. H. Pile.* J. Fr. Inst. [3] xxxii. 187.

—— On the variations of composition which the water of the Dead Sea appears to undergo: by *M. Boussingault.* Ann. Ch. Phys. [3] xlviii. 129.

—— Analysis of the bitter water of Mergentheim: by *J. Liebig.* Ann. Ch. Pharm. xcviii. 350.

—— On the subterraneous waters of Provence: by *M. de Villeneuve-Flayosc.* Compt. rend. xliii. 1032.

Water.—New process for estimating carbonic acid in mineral waters; with considerations on the constitution of the Vichy waters: by *H. Bingnet*. J. Pharm. [3] xxx. 321.

Wine.—On the chemical characters of red wines to which alum has been added; and application of these characters to the detection of small quantities of this salt introduced into the wine: by *M. Lassaigne*. Compt. rend. xlii. 410; Chem. Gaz. 1856, 136.

—— Note on the artificial colouring of wines: by *A. Chevallier*. J. Pharm. [3] xxix. 296.

—— On the use of burnt gypsum for clarifying turbid wines, preventing them from turning sour, and removing any acetic acid that may be present: by *Dr. Hessel*. Ann. Ch. Pharm. xcviii. 334.

Wood-vinegar.—On the presence of oxyphenic acid in wood-vinegar: by *M. Buchner*. Ann. Ch. Phys. [3] xlvi. 377.

Wool.—On the decoloration of silk and wool dyed with picric acid: by *C. Pugh*. J. pr. Chem. lxv. 368; Chem. Gaz. 1856, 297.

—— Testing of woollen tissues for intermixed cotton: by *A. Overbeck*. Chem. Gaz. 1856, 476.

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Zinc.—Expeditious method of assaying zinc ores. J. Pharm. [3] xxix. 205.

—— On two new crystalline compounds of zinc and antimony discovered by J. P. Cooke, Jun.: by *A. Kenngott*. Pogg. Ann. xcvi. 584.

—— On oxide of zinc: by *T. Morson*. J. Pharm. [3] xxx. 216.

—— On a process of engraving in relief on zinc: by *J. Devincenzi*. Compt. rend. xli. 1226; Phil. Mag. [4] xi. 167.

—— Preservation of animal substances by the saturated aqueous solution of sulphate of zinc: by *M. Strauss*. Durckheim. Compt. rend. xlii. 808.

Zirconia.—Zirconiferous tantalite from Limoges: by *G. Jenzsch*. Pogg. Ann. xcvii. 104.

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